

NOZZLE FLOWS WITH COUPLED VIBRATIONAL AND
DISSOCIATIONAL NONEQUILIBRIUM

by

DUVVURI TIRUMALESA

Manuscript received June 1966

Senior Research Fellow. On leave from the National Aeronautical
Laboratory, Bangalore, India, 1963 - 1965

AUGUST 1967

UTIAS REPORT NO. 123

ACKNOWLEDGEMENTS

The author wishes to thank Dr. G.N. Patterson for his encouragement and interest in the present work, Dr. I. I. Glass for many helpful discussions and critical comments, and Drs. J. E. Dove and P. A. Sullivan for a critical reading of the manuscript.

This work was supported by NASA under Grant NsG 633 and Canadian National Research Council and Defence Research Board. The author is indebted to the Faculty of Applied Science and Engineering for a Senior Research Fellowship.

SUMMARY

A detailed study is presented of one-dimensional, inviscid, nozzle flows with coupled vibrational and dissociational nonequilibrium. The ordinary coupled differential equations are integrated using the fourth order Runge-Kutta method on an IBM-7090 computer for several reservoir conditions. The method is used to predict the flow properties in the UTIAS 11" x 15" Hypersonic Shock Tunnel nozzle system. It is shown that the flow quantities are strongly dependent on the vibrational and dissociational models that are used in the analyses.

It was assumed that the vibrational state of the gas may be represented by a single vibrational temperature and that the effect of vibrational nonequilibrium on rates of dissociation may be taken into account by the introduction of a parameter which has the dimensions of temperature and which gives a higher probability for dissociation from higher vibrational energy levels. The dependence of this parameter on translational temperature is derived. However, in the calculations, an averaged constant value of this parameter is used as a simplification. The effect of dissociational nonequilibrium on vibrational relaxation is to modify the classical Landau-Teller equation by additional terms which take into account the average energy lost or gained due to dissociation and recombination. A qualitative study of the effects of the atom-molecule exchange reaction and relaxation from a higher to lower vibrationally excited state on the vibrational relaxation is carried out by shortening the vibrational relaxation times from those measured behind normal shocks.

The analysis has been successfully applied to predict the hypersonic nozzle test-section conditions for a newly developed UTIAS self-calibrating catalytic probe for measuring local atom concentrations in a dissociating oxygen flow.

TABLE OF CONTENTS

	<u>Page</u>
NOTATION	vi
1. INTRODUCTION	1
2. THERMODYNAMIC CONSIDERATIONS	2
3. RATE EQUATIONS	9
3.1 Chemical Reactions	9
3.1.1 Chemical Model	9
3.1.2 Collision Theory	13
3.1.3 Experimental rates	15
3.2 Vibrational Relaxation	15
3.2.1 No Dissociation	16
3.2.2 With Dissociation	16
3.2.3 Experimental Vibrational Relaxation Times	17
3.3 Model for the Present Calculations	18
3.3.1 Assumptions	18
3.3.1.1 Significance and Limitations of the Assumptions	19
3.3.2 Dissociational Rate Equation	22
3.3.3 Vibrational Relaxation Equation	23
4. BASIC EQUATIONS OF MOTION	23
4.1 Dissociational Models	24
4.1.1 Vibrational Nonequilibrium Models	24
4.1.1.1 Coupled Preferential Dissociation Model	24
4.1.1.2 Coupled Nonpreferential Model	26
4.1.1.3 Uncoupled Model	27
4.1.2 Vibrational Equilibrium Models	27
4.2 One Dimensional Flow	28
4.2.1 Effect of the Various Dissociation Models on Quasi-One Dimensional Flow Equations	29
4.2.2 Isentropic Limiting Flows	29

TABLE OF CONTENTS (con'd)

	<u>Page</u>
4. 2. 3 Determination of Mass Flow Under Nonequilibrium Conditions	31
4. 2. 4 Initial Conditions for Starting Nonequilibrium Flow Calculations	32
5. SPECIFIC CALCULATIONS	34
5. 1 Aims of the Calculations	34
5. 2 Expressions for Rate Constants	38
5. 3 Procedure for Numerical Calculations	39
5. 3. 1 Nonequilibrium Mass Flow	39
5. 3. 2 Passing Through the Critical Point $M_f = 1$	40
6. DISCUSSION OF RESULTS	41
6. 1 Axisymmetric Hyperbolic Nozzle	41
6. 1. 1 Effect of Starting Point for Nonequilibrium Calculations	41
6. 1. 2 Effect of the Relative Amount of Energy in Vibration	42
6. 1. 3 Importance of the Parameter U	43
6. 2 UTIAS 11" x 15" Hypersonic Shock Tunnel	45
6. 2. 1 Effect of Vibrational Relaxation Time τ_v	45
6. 2. 2 Effect of Variations in Reservoir Conditions	49
6. 2. 3 Realistic Set of U, τ_v Values	50
6. 3 Other Points of General Interest	50
6. 3. 1 Coupling Factor	51
6. 3. 2 Relaxation Lengths	51
7. CONCLUSIONS	57
8. SUGGESTIONS FOR FURTHER WORK	59
REFERENCES	60
APPENDIX A	64
APPENDIX B	71
APPENDIX C	88
APPENDIX D	92
APPENDIX E	114
FIGURES	

NOTATION

A	nozzle area ratio or Helmholtz free energy function.
A^*	nozzle area at the throat.
A_t, A_r, A_v	Helmholtz functions for thermodynamic subsystems consisting of translational, rotational and vibrational degrees of freedom respectively, given in Eqs. (A2), (A3).
A_{22}, A_{12}	Constants defined in Eqs. (B70), (B71).
a	constant in the rate expressions for dissociation Eq. (61) and vibration Eq. (81).
$a_f, a_{\bar{f}}$	frozen and partially frozen sound speeds.
a_i	stoichiometric coefficient for species i in the reaction equation (36).
b	constant in rate expression for vibration Eq. (81).
b_i	stoichiometric coefficient for species i in reaction equation (36).
b_0, b_1, b_2	constants in rate expression for vibration Eq. (D11).
c	constant in the expression for dissociation rate Eq. (B13).
D	dissociation energy.
d_0, d_1, d_2	constants in rate expression for dissociation Eq. (D10).
E	Total internal energy.
E'_v, E_v	vibrational energies evaluated at translational and vibrational temperatures Eqs. (74), (75).
E^*	activation energy for dissociation.
E_j	energy of vibrational level j
$\bar{E}_1, \bar{E}_2, \bar{E}$	average vibrational energies lost in dissociation by molecule-molecule, atom-molecule collisions and the sum of these defined in Eqs. (B44), (B45), (B46).
E_∞	vibrational energy evaluated at translational temperature.

e	Specific internal energy.
e_1, e_n, e_c	specific internal energy for the thermodynamic subsystems consisting of translational, internal, chemical modes of energy storage.
$f(t), f(r), f(v)$	partition functions for translational, rotational and vibrational degrees of freedom.
G	any extensive quantity of a volume element.
$\bar{G}_1, \bar{G}_2, \bar{G}$	average vibrational energies gained in recombination due to molecule-molecule, atom-molecule collision and the sum of these defined in Eqs. (B48), (B49), (B51).
g_i	partial specific quantities due to species i , defined in Eq. (6).
g_1, g_2	specific Gibbs potentials for atoms and molecules defined in Eqs. (A27), (A28).
g_{0j}	probability or statistical weight of ground energy level. ϵ_{0j} ($j = 1$ atoms, $j = 2$ molecules)
h	specific enthalpy or Planck constant.
$J_v = \frac{de_v}{dt} = \dot{e}_v$ $J_c = \frac{d\alpha}{dt} = \dot{\alpha}$	thermodynamic fluxes for vibration and dissociation.
j	vibrational energy level number.
K_1, K_2	constants defined in Eqs. (A29), (A30).
K_c	equilibrium constant Eq. (B85).
k	Boltzmann constant.
k_1, k_{-1}, k_2	reaction rates for reactions in Eq. (39), (48), (49).
k_d, k_r	dissociational and recombinational rate constants.
k_{da}, k_{dm}	rate constant for dissociation due to atom-molecule and molecule-molecule collisions respectively.
k_{dj}, k_{rj}	rate constants for dissociation from or recombination to vibrational level j .

k_{js}^m, k_{js}^a	rate constants for vibrational transitions from level j to s through collision with a molecule or an atom.
k_{10}	rate constant for transition from first excited level to ground state.
L	expression defined in Eq. (B38).
l	characteristic length.
M	Mach number.
m_a	mass of atoms per unit mole.
m_j	mass of a particle of species j ($j = 1$ atom, $j = 2$ molecule).
m_i	partial mass of species i .
m	mass flow in the nozzle.
N_j	number of particles of species j ($j = 1$ atom, $j = 2$ molecule) or number of molecules in vibrational energy level. j .
N	total number of particles of all species.
P	the probability for a reaction to occur in an energetic collision.
P_j	the probability for dissociation from vibrational level j in an energetic collision.
p	pressure.
Q	vibrational partition functions evaluated at various temperatures.
q	flow velocity.
R	gas constant per unit mass referred to diatomic gas.
Re	Reynolds number.
r	relaxation length.
s	specific entropy or exponent in the rate expression (64).
T	temperature.
t	time.

U	Parameter with dimensions of temperature used in the definition of P_j .
V	coupling factor, the ratio of dissociation rate constant for vibrational nonequilibrium and equilibrium.
x	distance along nozzle axis.
Z	total number of collisions per sec between n_A , n_B particles of type A and B in volume V.
Z_0	collision number of Z per cc per unit concentration.
Z_{dj} , Z_{rj}	fractional number of collisions leading to dissociation, from or recombination to vibrational level j .
Z_{022} , Z_{012}	collision number for molecule-molecule and atom-molecule collisions.
α	degree of dissociation (mass concentration of atoms).
δ^*	boundary layer displacement thickness.
ϵ_v , ϵ_∞	specific vibrational energy evaluated with vibrational and translational temperatures respectively.
ϵ_{0j}	excess energy of ground state of j species above reference energy level.
ζ	expression defined in Eq. (D41).
η	expression defined in Eq. (D57).
θ_r , θ_v , θ_d .	characteristic temperatures for rotation, vibration and dissociation respectively.
λ	relative efficiencies of atoms and molecules for causing dissociation, given in Eq. (B83).
μ	viscosity.
μ_i	chemical potential of species i.
ρ	density
ρ_D	characteristic dissociation density given in Eq. (A16).

σ_1, σ_2	collision cross-section for atoms and molecules.
τ_v	vibrational relaxation time.
$D\tau$	$= \tau_v \text{ expansion} / \tau_v \text{ normal shock.}$
ψ	expression defined in Eq. (B37).

Subscripts

o	stagnation or reservoir state.
d	dissociational.
t	translational.
v	vibrational.
e, eq. ∞	equilibrium flow conditions.
f, \bar{f}	frozen and partially frozen.
neq	nonequilibrium conditions.
r	reference state or recombinational.
i	of chemical species i or thermodynamic subsystem i.

Superscript

+	activated complex.
---	--------------------

I. INTRODUCTION

At present, expansion flows of reacting gases at high temperatures are calculated with the following gas models, which are listed in order of increasing complexity:

I. Ideal or Lighthill dissociating gas for pure diatomic gases, where vibration is considered to be excited to half its classical value, with dissociational nonequilibrium; (e. g. Refs. 1-4).

II. Vibration in equilibrium with translation and rotation, and with dissociational nonequilibrium (e. g. Refs. 5-12).

III. Simultaneous and independent vibrational and dissociational nonequilibrium. (Refs. 13-17).

In all these calculations, the vibrational relaxation times and dissociational and recombinational rate constants used are those determined behind normal shocks. The vibrational relaxation times are determined in the absence of dissociation, while dissociational and recombinational rate constants correspond to a situation where the vibration reaches equilibrium with translation. The modification of the rate constants in the dissociational rate equation, when vibration has not reached equilibrium with translation, was considered in Ref. 18. Modification of this type was first used for flows behind normal shocks by Hammerling, Teare, Kivel (Ref. 19). This model was further extended to take into account the inverse effect of dissociational nonequilibrium on vibrational relaxation, for flow behind normal shocks by Treanor and Marrone (Refs. 20-22).

In addition, recent experiments in nozzle expansion flows (Ref. 23) appear to indicate that the vibrational relaxation times calculated by using the classical Landau-Teller model may be shorter in such flows compared with those behind normal shocks. Consequently, a realistic gas model has to take into account all of these factors.

Glass and Takano (Ref. 5), in their calculations of expansion flow of dissociated oxygen around a corner with model (II), found the occurrence of a deexcitation shock behind the expansion fan and noted that this might not have occurred if a proper vibrational relaxation rate equation had been used.

Also, a probe has been developed at UTIAS for direct measurement of atomic mass fraction in UTIAS hypersonic shock tunnel. Since the coupling of vibrational and dissociational nonequilibrium will have an important effect on the flow properties of the gas in the test section, in particular on the frozen atomic mass fraction, it is proposed to consider the effect on expansion flows in nozzles to give a realistic theoretical estimate of the flow properties in the test section.

2. THERMODYNAMIC CONSIDERATIONS

In dealing with any nonequilibrium system, the postulate of local equilibrium is used. This postulate states:

Postulate I

"For a system in which irreversible processes are taking place, all thermodynamic functions of state exist for each element of the system. These thermodynamic quantities for the nonequilibrium system are the same functions of the local state variables as the corresponding equilibrium thermodynamic quantities". (Ref. 24).

For a gaseous system consisting of r chemical components the fundamental state variables may be taken as the mass density ρ of a volume element dV , the partial mass densities ρ_i of the r chemical components giving the composition of this volume and the specific internal energy e of this volume element. We have, of course:

$$\sum \rho_i = \rho \quad (1)$$

For a nonequilibrium system e , ρ_i , ρ depend on the position \vec{r} in space and on time t i.e.

$$e = e(\vec{r}, t) \quad (2)$$

$$\rho_i = \rho_i(\vec{r}, t) \quad (3)$$

$$\rho = \rho(\vec{r}, t) \quad (4)$$

Now the postulate of local equilibrium says that all thermodynamic quantities for a nonequilibrium system may be defined by the same functional dependence on ρ , ρ_i , e as is given by measurements on equilibrium systems. For example, the local temperature $T(\vec{r}, t)$ may be defined by the same function $T(\frac{p}{\rho}, e)$ as in equilibrium, and so is the local pressure $p(\vec{r}, t)$. The specific entropy S is defined by the Gibb's equation

$$de = Tds - p d(\frac{1}{\rho}) + \sum \mu_i d(\frac{\rho_i}{\rho}) \quad (5)$$

where μ_i is the chemical potential or partial specific Gibb's free energy of component i .

Further the partial specific quantities \bar{g}_i in an arbitrary volume element dv of a nonequilibrium system are defined by the equilibrium relation

$$\bar{g}_i = \left(\frac{\partial G}{\partial m_i} \right)_{p, T, m_{j \neq i}} \quad (6)$$

where G represents any extensive quantity of the volume element dv and m_i is the mass of component i in dv . From this relation, one obtains for the relations between the specific quantities

$$e = \sum \frac{\rho_i}{\rho} \bar{e}_i \quad (7)$$

$$\bar{S} = \sum \frac{P_i}{P} \bar{S}_i \quad (8)$$

$$\bar{e} = T \bar{S}_i - P \bar{V}_i + u_i \quad (9)$$

$$\bar{h}_i = \bar{e}_i + P \bar{V}_i \quad (10)$$

or
$$\bar{h}_i = T \bar{S}_i + u_i \quad (11)$$

At this point it is necessary to consider the meaning of temperature for a system in simultaneous vibrational and dissociational nonequilibrium. For simplicity, consider the case of a dissociating pure diatomic gas such that the system consists of a binary mixture of atoms and molecules. For such a mixture, the specific internal energy e , temperature T and atomic mass fraction α are related in thermodynamic equilibrium through

$$e = e_{tr+rot} + e_{vib} + e_{diss} \quad (12)$$

$$e = \frac{5+\alpha}{2} RT + (1-\alpha) R \epsilon_v + \alpha R \theta_d$$

where R is the gas constant referred to the diatomic gas and ϵ_v is the vibrational energy which can be expressed for equilibrium in terms of T by

$$\epsilon_v = \theta_v / [\exp(\frac{\theta_v}{T}) - 1] \quad (13)$$

and θ_v , θ_d are the characteristic temperatures for vibration and dissociation respectively. In the case of vibrational nonequilibrium, the vibrational energy ϵ_v cannot be written so explicitly in terms of the temperature T and may have to be treated as one of the independent variables. Under the above postulate, the local temperature will be defined by Eq. (12) along with Eq. (13) for the vibrational energy at equilibrium, or one may write T as the solution of the equation

$$\frac{5+\alpha}{2(1-\alpha)} \cdot \frac{1}{Z} + \frac{1}{e^Z - 1} = \frac{1}{(1-\alpha)R\theta_d} [e - \alpha\theta_d R] = \frac{e_{tr+rot} + e_{vib}}{(1-\alpha)R\theta_d} \quad (14)$$

where $Z = \theta_v/T$. The three terms in Eq. (12) may be identified as the

contributions to the energy from translational-rotational, vibrational and dissociational degrees of freedom of the whole system. Thus Eq. (14) will imply that in the definition of temperature, the dissociative part of the energy need not be considered. If E_v is taken as an independent parameter for vibrational nonequilibrium, one may further define a temperature

$$T = \frac{2}{(5+2)R} [E - (1-\alpha)RE_v - \alpha R\theta_D]$$

$$= \frac{2}{(5+2)R} E_{tr+rot} \quad (15)$$

If the vibrational contribution E_{vib} to the total specific internal energy E can be expressed in terms of E_v defined by Eq. (13) with the same T as in Eq. (12), then the temperatures defined by Eqs. (14) and (15) become identical. This is the case when there is vibrational equilibrium but dissociational nonequilibrium. When E_{vib} cannot be so expressed, the temperature defined by Eqs. (14) and (15) will be different, and according to the postulate I, the temperature defined by Eq. (14) has to be taken as the proper one. Eq. (13) can also be solved for another temperature. Let the temperatures obtained as solutions of Eqs. (13), (14) and (15) be denoted by T_v , T' and T_t . In thermodynamic equilibrium the relation between pressure, density and temperature is

$$P = \rho RT(1+\alpha) \quad (16)$$

By using the three different temperatures, one will get three different pressures P_v , P' , P_t respectively. Which of these pairs of T , p , are to be used in Eqs. (5), (9), (10), (11)?

Wood and Kirkwood (Ref. 25) circumvented this difficulty by modifying the postulate I as follows:-

"The assumption of local thermodynamic equilibrium within classes of the degrees of freedom of the system is made, but it is supposed that the attainment of equilibrium between these classes is governed by rate processes which can be stated in terms of state variables characterizing the partial equilibrium of various classes. The assumption of equilibrium within each class means that (classically speaking) a Boltzmann distribution exists for each and consequently a temperature and entropy, as well as energy, may be defined for each class". For a further discussion of some of these points consult pp's 165-170 of Ref. 43.

It is assumed in this analysis, that the translational degrees of freedom of all species constitute a single class and the corresponding temperature, energy, entropy and chemical potential T , E , S , μ_{ij} satisfy Eq. (5) i.e.

$$dE = T_1 dS_1 - P d(1/\rho) + \sum \mu_{ij} d(P_i/P) \quad (17)$$

whereas the equilibrium states of all other classes, called internal classes, are assumed to be specified by their respective temperatures T_n ($n \geq 2$) and the composition variables P_i alone, such that for these classes Eq. (5) may be written as

$$de_n = T_n dS_n + \sum \mu_{i,n} d(P_i/p) \quad n \geq 2 \quad (18)$$

Thus for the total energy change de of the system Eqs. (17) and (18) yield

$$de = \sum_n T_n dS_n - p d(\frac{1}{p}) + \sum_n \sum_i \mu_{i,n} d(\frac{P_i}{p}) \quad (19)$$

Since the pressure p enters only in Eq. (17) for translational degrees of freedom, the translational temperature T_t and the corresponding pressure P_t are the set to be used in Eq. (16). The rate processes for the attainment of equilibrium between these various classes are taken to be of the form

$$\frac{dT_n}{dt} = Q_n \quad (n \geq 2) \quad (20)$$

where Q_n is a function of the local thermodynamic state. These other internal classes may be taken as rotational and vibrational degrees of freedom while the chemical nonequilibrium is taken to be described by

$$\frac{d(P_i/p)}{dt} = W \quad (21)$$

It was pointed out by Wood and Kirkwood, that this theory is not a microscopic one and this, does not provide a recipe for classification of the degrees of freedom. This classification is to be done independently of this theory. For example, the above classification of translational and internal degrees of freedom as separate classes may be considered to be obtained from a statistical description of the various modes of energy storage. Heims (Ref. 16) pointed out that for a vibrating, dissociating gas, to specify the properties of the gas completely, it is necessary to specify the internal energy as in Eq. (12) with E_v as an additional independent variable, together with the equation of state (16), where T is the translational temperature. This implies that the pressure of the gas comes from translational motion only. Starting with these two equations and the differential flow relations, he shows that the entropy S is an exact differential of the variables T_t , p , $\alpha = P_{atm}/p$, $E_v = E_v = (1-\alpha)E_v R$. For adiabatic flow, the entropy change due to the irreversible relaxation processes was shown to be

$$ds = de_v \left(\frac{1}{T_v} - \frac{1}{T_t} \right) + d\alpha \left[\log \frac{(1-\alpha)\sqrt{T}(1-e^{q/T_v})}{p\alpha^2} - \frac{1}{T_t} \right] \quad (22)$$

Now, when there are two heat reservoirs at temperatures T_1 and T_2 and an energy flow between them such that system '1' changes its energy by de , then the overall entropy increase is

$$ds = de \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (23)$$

Heims pointed out that the relaxation process is analogous to heat flow, energy being interchanged between "systems of vibrations at temperature T_v "; "systems of translational motions at temperature T_t " and the "chemical system" at a chemical temperature $T_c = \left[\log \frac{(1-\alpha)\sqrt{T}(1-e^{-\theta_v/T_v})}{P\alpha^2} \right]^{-1}$

But, this is exact only for vibrational relaxation without reaction, and not when reaction is occurring. This is so, since in the case of reaction occurring, the chemical temperature is dependent on T_v as well as T_t .

Another important point brought out in Heim's analysis is the relation between vibrational relaxation rate and rate of chemical reaction. The right hand side of Eq. (22) is seen to be composed of the sum of two products. In the notation of irreversible thermodynamics (Ref. 24), $\frac{de_v}{dt}$ and $\frac{d\alpha}{dt}$

are "Fluxes" (J_v, J_c) and the coefficients of de_v and $d\alpha$ in Eq. (22) are the corresponding forces (X_v, X_c) and the theory yields a relation between $\dot{e}_v = \frac{de_v}{dt}$ and $\dot{\alpha} = \frac{d\alpha}{dt}$, known as the Onsager reciprocal relation, namely,

$$\left(\frac{\partial \dot{\alpha}}{\partial X_v} \right)_{eq} = \left(\frac{\partial \dot{e}_v}{\partial X_c} \right)_{eq} \quad (24)$$

where the subscript eq. means that the derivatives are taken at equilibrium. Eschenroeder (Ref. 26), uses the concept of chemical temperature, namely

$$T_c = \left[\log \frac{(1-\alpha)\sqrt{T}(1-e^{-\theta_v/T_v})}{P\alpha^2} \right]^{-1} \quad (25)$$

for vibrational equilibrium and chemical nonequilibrium to evaluate entropy rise by the equation

$$ds = de_c \left(\frac{1}{T_c} - \frac{1}{T} \right) \quad (26)$$

where de_c is the heat released or absorbed by the reaction for the gas model of Lighthill. For this model, Eq. (25) is written as

$$T_c = \left[\log \frac{(1-\alpha)}{P'\alpha^2} \right]^{-1} \quad (27)$$

where

$$\rho' = \frac{\rho}{\rho_{DL}} \quad (28)$$

and

$$\rho_{DL} = 2\rho_D \left(\frac{\theta_v}{T}\right)^{1/2} (1 - e^{-\theta_v/T}) \quad (29)$$

ρ_D being the characteristic dissociation density.

Mates and Weatherstone (Ref. 27) examined the justification for using the concept of multiple temperatures from a classical thermodynamic point of view, to reconcile the analyses of Heims and Eschenroeder. They conclude that the classical thermodynamic temperature can sometimes be used to characterize a particular degree of freedom, such as vibration, even if it is not in equilibrium with the other degrees of freedom. But the same is not true with chemical temperature, except for chemical systems in which the reactant and products have equal constant volume mass specific heats. An example of such a system is the ideal dissociating gas of Lighthill.

From all these analyses it would appear that for a gas in chemical and thermal nonequilibrium, some use of statistical thermodynamics is necessary before one can use the classical thermodynamic relations involving only macroscopic variables. For example, the classification of subsystems in the analysis of Wood and Kirkwood and division of energy into different modes in the analysis of Heims are statistical concepts.

Thus in the present analysis, the following assumptions will be made:-

- I) The molecular transport effects leading to viscosity, heat conduction and diffusion are neglected.
- II) The system may be considered to consist of subsystems characterised by the translational, rotational and vibrational degrees of freedom.
- III) Even though the total system is in nonequilibrium, there is equilibrium within the subsystems. Specifically, the translational and rotational degrees of freedom are in equilibrium within themselves and with each other such that they may be specified by Boltzmann distributions in terms of a single parameter, namely the translational temperature T_t . The vibrational subsystem is assumed to be also specified by a Boltzmann distribution in terms of a parameter, namely vibrational temperature T_v .
- IV) The intensive properties such as density, enthalpy, etc. for the mixture are the weighted sums of the corresponding properties for the single system.
- V) The Helmholtz free energy function may be written in terms of these temperatures for the whole system from the statistical thermodynamics and

all the other thermodynamic functions like entropy, internal energy, pressure, etc. can be obtained by the classical thermodynamic relation.

It was shown by Treanor (Ref. 28) that for simultaneous vibrational and dissociational nonequilibrium, the vibrational distribution tends to deviate more and more from a Boltzmann distribution with increasing translational temperature. However, for the range of temperatures of interest here (around 5000°K), this deviation seems to be quite predominant only at higher vibrational energy levels. Thus for simplicity, assumption III, is made about vibrational temperature.

It was pointed out in Ref. 16 that the electronic partition functions f_{e_1} and f_{e_2} for the oxygen atom and molecule respectively may be taken as constant for the temperature range 1500°K to 8000°K, and that these constants are approximately equal to the degeneracy of the ground state of atom or molecule, namely, g_{o_1} and g_{o_2} of Appendix A. For this temperature range the use of values $f_{e_1} = 8.8$ and $f_{e_2} = 3.3$ gives P_n of Appendix A within 5 percent and α_e within 2.5 percent. See note (I) Appendix E.

The thermodynamic functions for the gas model considered are derived in detail in Appendix A. They are Eqs. (A18), (A22), (A23), (A27), (A28), (A31),

Specific internal energy:

$$e = R \left[\frac{5+\alpha}{2} T_t + (1-\alpha) \frac{\theta_v}{e^{\theta_v/T_v} - 1} + \alpha \theta_D \right] \quad (30)$$

Specific enthalpy:

$$h = R \left[\frac{7+\alpha}{2} T_t + (1-\alpha) \frac{\theta_v}{e^{\theta_v/T_v} - 1} + \alpha \theta_D \right] \quad (31)$$

Pressure:

$$p = P R T_t (1 + \alpha) \quad (32)$$

Specific entropy:

$$\begin{aligned} \frac{S - S_n}{R} = & \frac{3\alpha}{2} + \frac{(1-\alpha)E_v}{T_v} + (1+\alpha) \frac{\theta_D}{T_t} + 2 \log \left[\frac{T_t}{T_r} \frac{\alpha}{(1-\alpha)(1-e^{-\theta_v/T_v})} \right] \\ & + (1+\alpha) \log \left[\frac{2P_D}{P} \left(\frac{T_t}{\theta_v} \right)^{3/2} e^{-\theta_v/T_t} (1-e^{-\theta_v/T_v}) \frac{(1-\alpha)}{\alpha^2} \right] \end{aligned} \quad (33)$$

Specific chemical potentials:

for atoms:-

$$g_1 = R \theta_D - R T_t \log \left(\frac{K_1 T_t^{3/2}}{P \alpha} \right) \quad (34)$$

for molecules:-

$$g_2 = -RT_t \log \left[K_2 \frac{T^{\frac{5}{2}}}{P(1-\alpha)} \right] - RT_v \log (1 - e^{-\theta_v/T_v})^{-1} \quad (35)$$

where constants K_1 , K_2 , S_v are defined by Eqs. (A29), (A30), (A17) respectively, R is gas constant per unit mass of the diatomic gas, α atomic mass fraction, θ_v , θ_d are the characteristic temperatures for vibration and dissociation, T_t , T_v are the translational and vibrational temperatures and E_v is the vibrational energy defined by Eq. (13) with $T = T_v$.

3. RATE EQUATIONS

3.1 Chemical Reactions:-

In all the studies involving chemical reactions referred to in the introduction, for a reaction equation of the type



where x_i denote the chemical species and a_i , b_i are the stoichiometric coefficients of the reactants and products respectively, it is assumed that the rate of reaction for species x_i may be written as

$$\frac{d[x_i]}{dt} = k_d \prod [x_i]^{a_i} - k_r \prod [x_i]^{b_i} \quad (37)$$

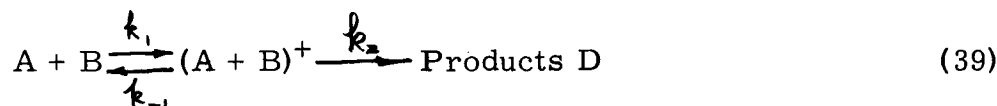
where Π denotes the product and k_d , k_r are considered to be dependent on temperature alone and not on concentrations. But there appear to be circumstances when this is not true. A short discussion of chemical ideas concerning these rates will clarify the point.

3.1.1. Chemical Model:-

In the study of chemistry, reactions are considered to occur through what are called activated complexes. For simplicity consider at constant temperature, the reaction



The process is then written as



where $(A+B)^+$ is an activated complex of A and B . There are two theories

describing the relation between $(A+B)^+$ and the reactants and products, namely I) Equilibrium theory and II) Steady state theory (Refs. 29, 30).

I) Equilibrium rates:-

In this analysis it is supposed that the reactants and the activated complexes are in equilibrium with each other, and that the rates of the three reactions indicated in Eq. (39) may be written as the product of concentrations times a constant which is dependent on temperature alone. For example,

$$\frac{d[(A+B)^+]}{dt} = k_1[A][B] - k_{-1}[(A+B)^+] \quad (40)$$

for the first part of the reaction and

$$\frac{d[D]}{dt} = k_2[(A+B)^+] \quad (41)$$

for the second part of the reaction. From the assumption of equilibrium of the first part of the reaction, equating Eq. (40) to zero and then solving for $(A+B)^+$ and substituting in Eq. (41), one can write for the reaction of Eq. (38),

$$-\frac{d[A]}{dt} = \frac{d[D]}{dt} = k_d[A][B] = k_2 \frac{k_1}{k_{-1}} [A][B] \quad (42)$$

giving

$$k_d = k_2 \frac{k_1}{k_{-1}} = f(T) \quad (43)$$

such that k_d is a function of temperature alone since k_1 , k_{-1} , k_2 are assumed to be functions of temperature alone.

II) Steady state rates:-

In this analysis, no equilibrium is assumed between the activated complexes and reactants. It is assumed that the activated complexes exist for a short time interval after formation, and then either they become products or return to the reactant state.

It is again assumed that the rates of the elementary reactants can be written as in Eqs. (40), (41). For the steady state equation, one has

$$\frac{d[(A+B)^+]}{dt} = k_1[A][B] - k_{-1}[(A+B)^+] - k_2[(A+B)^+] = 0 \quad (44)$$

or

$$[(A+B)^+] = \frac{k_1}{k_{-1} + k_2} [A][B] \quad (45)$$

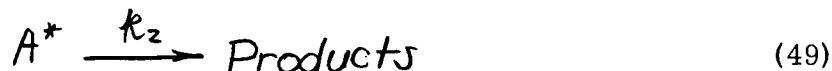
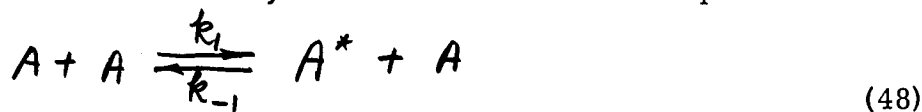
or

$$\frac{d[D]}{dt} = k_2 [(A+B)^+] = \frac{k_1 k_2}{k_{-1} + k_2} [A][B] = k_d [A][B] \quad (46)$$

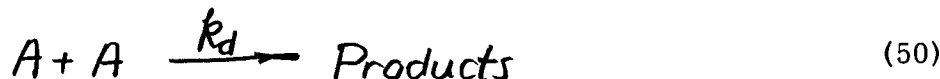
$$k_d = \frac{k_1 k_2}{k_{-1} + k_2} \quad (47)$$

III) Dissociation of Diatomic molecule:-

For molecular dissociation, the reaction is known to proceed in two steps



which replace



In the Equilibrium assumption, one finds

$$k_1 [A]^2 - k_{-1} [A^*][A] = 0$$

$$[A^*] = \frac{k_1}{k_{-1}} [A]$$

$$-k_d [A]^2 = \frac{d[A]}{dt} = -\frac{d[A^*]}{dt} = -k_2 [A^*] = -\frac{k_2 k_1}{k_{-1}} [A] \quad (51)$$

or

$$k_d = \frac{k_2 k_1}{k_{-1} [A]}$$

with the steady state assumption

$$k_1 [A]^2 - k_{-1} [A^*][A] - k_2 [A^*] = 0$$

$$[A^*] = \frac{k_1}{k_{-1} [A] + k_2} [A]^2$$

$$-k_d [A]^2 = \frac{d[A]}{dt} = -\frac{d[A^*]}{dt} = -k_2 [A^*] = \frac{-k_1 k_2}{k_{-1} [A] + k_2} [A]^2 \quad (52)$$

or

$$k_d = \frac{k_1 k_2}{k_{-1}[A] + k_2}$$

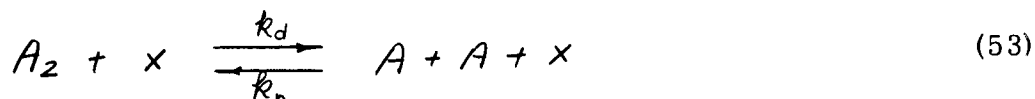
This it would appear that rate coefficients k_d are dependent on concentration as well as on temperature. One important point to be noted is that the final stage, that is Eq. (49) is supposed to occur without any further collisions, but by only a reshuffling of the energy in the various internal modes to the bond that is to be broken. Thus, in a complex molecule with several vibrational modes, the energy acquired by collisions may be initially distributed in such a way that it is not immediately transferred to the bond that breaks ultimately and some time may elapse before, if ever, this event takes place.

Another interesting point to be noted is that the equilibrium assumption for the rates of a diatomic molecule means that one may assign a vibrational temperature T_v to indicate the vibrational energy distribution in various levels. This may be visualised by considering A and A* as ground and excited vibrational states. This temperature may or may not be in equilibrium with the translational temperature T_t . In the latter case, the coefficients k_1 , k_{-1} , k_2 in Eqs. (51), (52) will have to be dependent on T_t as well as T_v and consequently, so will k_d .

The steady state assumption for diatomic molecules means that no equilibrium within the vibrational degrees of freedom can be assumed that is, there is a non-Boltzmann distribution in vibration. In the present report, the rate coefficients will thus be equilibrium rates in the chemical language because of the assumption of Boltzmann distribution in vibration. The dissociation mechanism is discussed in more detail in Appendix E.

IV) Rate Coefficients:-

Thus for a dissociating diatomic gas following the reaction



where x may be either an atom or molecule, the net rate of reaction may be written as

$$\frac{d[A_2]}{dt} = -k_d[A_2][x] + k_r[A]^2[x] \quad (54)$$

where k_d and k_r are called the rate constants and are temperature dependent only. They are also called rate coefficients or specific rates. If Z_d and Z_r are the number of dissociations and recombinations per cc per sec, then

$$\frac{d[A_2]}{dt} = -Z_d + Z_r \quad (55)$$

$$Z_d = k_d [A_2] [x] \quad (56)$$

and

$$Z_r = k_r [A]^2 [x] \quad (57)$$

$$k_d = \frac{Z_d}{[A_2] [x]} \quad (58)$$

or

$$k_r = \frac{Z_r}{[A]^2 [x]} \quad (59)$$

The ratio of these forward and backwards rate coefficients k_d/k_r is thus dependent upon temperature only and this ratio is known as the equilibrium constant K_c since at chemical equilibrium $Z_d = Z_r$ and this ratio is

$$K_c = \frac{k_d}{k_r} = \left(\frac{[A]^2}{[A_2]} \right)_{eq} \quad (60)$$

K_c can be calculated from statistical mechanics (Refs. 29, 30). Arrhenius was the first to investigate the temperature dependence of k_d experimentally and proposed an exponential dependence on temperature. It is now usual to assume:

$$\begin{aligned} k_d &= A(T) e^{-E^*/kT} \\ &= a T^n e^{-E^*/kT} \end{aligned} \quad (61)$$

where E^* is the activation energy and is normally taken to be equal to the dissociation energy D for diatomic molecules.

Finally one has,

$$k_d = a T^n e^{-D/T} \quad (62)$$

where a and n are empirical constants. This expression for k_d can also be derived using Thermodynamic considerations (Refs. 29, 30).

3.1.2. Collision Theory:-

Let n_A and n_B be the number densities of molecules of type A and type B. Let z be the number of collisions per cc per sec. between these two types of molecules. In the simplest model for reaction, it is assumed that the reaction occurs whenever collision occurs with particles in an activated or

energised state, that is with an energy greater than or equal to the activation energy. Then the number of reactions per cc per sec. may be written as

$$Z_d = Z e^{-E^*/RT} \quad (63)$$

where the factor $e^{-E^*/RT}$ is that fraction of all collisions for which the kinetic energy of relative translational motion along the line of centres at the moment of impact exceeds E^* . The quantity E^* is known as the activation energy and is in general assumed to be the dissociation energy. In this model only the translational energy of the molecules is taken into account. As this prediction does not agree with observed reaction rates, a probability factor P is added. In addition all the degrees of freedom of the colliding partners, like vibrational and rotational, are also taken into account giving finally, (Ref. 31)

$$Z_d = P \cdot Z \frac{(E^*/RT)^s}{s!} e^{-E^*/RT} \quad (64)$$

where

P is the probability for the reaction to occur
 Z is the number of collisions per cc per sec between the n_A, n_B number of molecules of types A and B,
 E^* is the activation energy or the minimum total energy necessary for reaction to occur, taken to be equal to the dissociation energy D ,
 T is the temperature of the gas mixture,
 s is the factor that takes into account the internal degrees of freedom of the particles entering in collision and is shown to be 1 for diatomic molecule-atom collisions and 2 for diatomic molecule-molecule collisions.

In the derivation of Eq. (64) it is assumed that the vibration is in equilibrium with rotational and translational degrees of freedom.

Equilibrium Rates:-

For reaction between molecules A and B, the equilibrium rates, that is rates for the activated complexes being in equilibrium with unactivated molecules, are written in terms of partition functions with the aid of statistical mechanics as (Ref. 30)

$$\frac{Z_d}{N_A N_B} = k_d = P \frac{RT}{h} \cdot \frac{Q^+}{Q_A Q_B} e^{-E^*/RT}$$

where Q^+ = partition function for activated complex $(A + B)^+$
 Q_A = partition function for molecule A
 Q_B = partition function for molecule B

P = probability of reaction occurring
 k, h = Boltzmann and Planck constants respectively
 E^* = activation energy
 N_A, N_B = number densities of molecule of type A and B respectively.

For diatomic molecule-molecule collisions,

$$Q_A = Q_B = f^{(t)} f^{(r)} f^{(v)}$$

$$Q^+ = f^{+(t)} f^{+(r)} f^{+(v)}$$

where $f^{(t)}, f^{(r)}, f^{(v)}$, are the translational, rotational and vibrational partition functions.

Steady State Rates:-

For steady state rates, Eq. (64) is obtained (see Ref. 30 for further details).

3.1.3 Experimental rates:-

In the determination of rate coefficients k_d, k_r at high temperatures, the rates are assumed to be of the form given by Eq. (64) and the values of P and s are determined by the study of density profiles behind normal shocks in shock tubes (for example Refs. 32, 33, 34). It appears that in almost all these studies, by the time dissociation begins vibration has already reached equilibrium with rotation and translation (for example Ref. 32, 33) whereas in some experiments of Wray (Ref. 34) for dissociation of oxygen in an oxygen-argon mixture, there appears to be an overlap region where vibration and dissociation are taking place simultaneously.

In a nozzle flow, there is simultaneous vibrational and dissociational non-equilibrium. Thus the rate constants for dissociation as determined behind shock fronts (which are essentially for vibrational equilibrium) are to be modified for the vibrational nonequilibrium.

3.2 Vibrational relaxation:-

The vibrational relaxation equation can be derived by using rate equations which are similar in form to those used for chemical reaction by considering the molecules in different energy levels to be different species, namely,



where A_m is a molecule in any vibrational level

$$\frac{d[A_j]}{dt} = - \sum_m k_{js}^m [A_j][A_m] + \sum_n k_{sj}^n [A_s][A_n] \quad (66)$$

3.2.1. No dissociation:-

When there is no dissociation, one has to consider only Eq. (66) which may be written

$$\begin{aligned}\frac{d[A_j]}{dt} &= -[A_j] \left(\sum_m k_{js}^m [A_m] \right) + [A_s] \left(\sum_n k_{sj}^n [A_n] \right) \\ &= -[A_j] k_{js} [A_2] + [A_s] k_{sj} [A_2]\end{aligned}\quad (67)$$

The Landau-Teller equation for vibrational relaxation for a system of harmonic oscillators in terms of the vibrational energy

$$E_v = h\nu \sum_j j [A_j] \quad (68)$$

is obtained from Eq. (67) by multiplying by $E_j = j h\nu$ and summing over the levels and applying the rules

$$k_{js} = 0 \quad \text{for } |j-s| \neq 1 \quad (69)$$

$$k_{j,j-1} = j k_{10} \quad (70)$$

$$k_{j,j+1} = (j+1) k_{01} = (j+1) k_{10} \exp\left(-\frac{h\nu}{kT}\right) \quad (71)$$

this gives

$$\begin{aligned}\frac{dE_v}{dt} &= k_{10} \left[1 - \exp\left(-\frac{h\nu}{kT}\right) \right] (E'_v - E_v) \\ &= (E'_v - E_v) / \tau_v\end{aligned}\quad (72)$$

wherein a vibrational temperature T_v is defined such that

$$\begin{aligned}[A_j] &= \exp(-j h\nu / kT_v) \\ &= \exp(-j \theta_v / T_v)\end{aligned}\quad (73)$$

giving

$$E_v = k\theta_v / [\exp(-\theta_v / T_v) - 1] \quad (74)$$

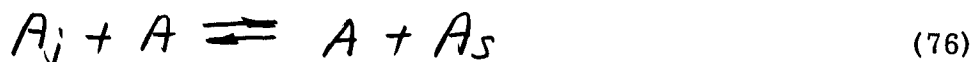
and E'_v is defined as

$$E'_v = k\theta_v / [\exp(-\theta_v / T_e) - 1] \quad (75)$$

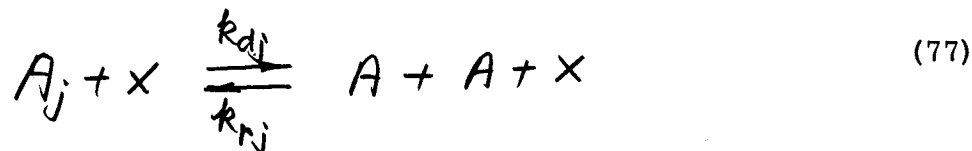
3.2.2 With dissociation:-

When dissociation and recombination are occurring, one has to write two

more reactions,



which gives relaxation by exchange of partners, and



which takes into account change in A_j due to recombination and dissociation by collision with a partner X which may be an atom or a molecule. The rate equations for reactions (76), (77) may be written as

$$\frac{d[A_j]}{dt} = -k_{js}^a [A_j][A] + k_{sj}^a [A][A_s] \quad (78)$$

$$\frac{d[A_j]}{dt} = -k_{dj} [A_j][X] + k_{rj} [A]^2 [X] \quad (79)$$

Thus the net change in $[A_j]$ due to all these reactions is obtained by adding Eqs. (67), (78), (79) as

$$\begin{aligned} \frac{d[A_j]}{dt} = & -k_{js} [A_j][A_2] + k_{sj} [A_s][A_2] - k_{js}^a [A_j][A] \\ & + k_{sj}^a [A][A_s] - k_{dj} [A_j][X] + k_{rj} [A]^2 [X] \end{aligned} \quad (80)$$

Eq. (80) gives all the information needed for calculating the vibrational and dissociational nonequilibrium provided one knows various rate constants. As these rate coefficients are not known in the present state of knowledge, the only alternative is the simplification of this equation under suitable assumptions about the rate coefficients.

3.2.3 Experimental vibrational relaxation times:-

The vibrational relaxation times were found theoretically and experimentally for a number of gases by experiments behind normal shocks (see Ref. 35 for comparison between theory and experiment). It was found in general that for diatomic gases the product $\tau_v p$ where p is the pressure may be written as a function of temperature (Ref. 36).

$$\tau_v p = a \exp(-b T_t^{-1/3}) \quad (81)$$

where a and b are constants and T_t is temperature.

It appears that the vibrational relaxation times calculated through the use of Landau-Teller equation for expansion of nitrogen in nozzles are much shorter than those determined behind normal shocks (Ref. 23). Treanor (Ref. 28) using the steady state assumption (that is relaxation from an initial non-Boltzmann like distribution) tried to see if this phenomenon could be explained, but not with great success. At present no further results are available on this point.

Some theoretical calculations were made by Alterman and Wilson (Ref. 37) for vibrational energy transfer for atom-diatom molecule collisions. Their calculations show that the vibrational relaxation times for molecules, having a given vibrational energy initially are substantially shorter than for the case when the molecules have no vibrational energy initially. Extending their conclusions a little further by assuming that a similar result may be expected for molecule-molecule collisions and also for relaxation from lower to higher or higher to lower vibrational energies (as in shocks and expansions respectively), there seems to be some theoretical justification of shorter vibrational relaxation times in expansions than behind shocks even if one does not assume relaxation from a steady state non-Boltzmann distribution of vibrational energy. Unfortunately, the calculations of Ref. 37 are for $Xe - Br_2$ collisions and no relative values of the vibrational relaxation times for the two cases are given. Also Wild (Ref. 38) has shown theoretically that the relaxation time is also a function of the vibrationally excited state of the gas.

3.3 Model for the present calculations:-

For an exact calculation of the simultaneous vibrational and dissociational relaxation, one has to use a system of equations of type Eq. (80) for the several vibrational levels of the molecule. The problem is made more difficult since none of the details of these rate coefficients are known. In fact, in the literature, the reaction (76) of vibrational relaxation due to atom exchange is not even discussed and there is no information on k_{js}^a, k_{sj}^a . As for the other rate coefficients, only the overall rates, namely, τ_v , k_d , k_r the vibrational relaxation time where there is no dissociation, and k_d , k_r the dissociational and recombinational rate coefficients with vibrational equilibrium are known. An attempt is made to simplify the set of simultaneous equations (80) to two equations, one for the net rate of change of the vibrational energy in a modified Landau-Teller form and the other for the net rate of change of molecules or the dissociation rate equation in the form of Eq. (54) where k_d and k_r are modified. For example by taking the sum of Eq. (80) over all vibrational energy levels, one obtains the overall rate equation for the net rate of change of molecules. Multiplying Eq. (80) with the vibrational energy appropriate to level j and summing over all the vibrational energy levels one obtains the overall rate equation for the net rate of change of the total vibrational energy.

3.3.1 Assumptions:-

The equation for the net rate of change of molecules in level j (Eq. (80)), may be written in a slightly modified form as

$$\frac{d[A_j]}{dt} = -k_{js}[A_j][A_2] + k_{sj}[A_s][A_2] - k_{js}^a[A_j][A] + k_{sj}^a[A][A_s] - Z_{dj} + Z_{rj} \quad (82)$$

where Z_{dj} and Z_{rj} are dissociation and recombination rates into level j .

The assumptions made in simplifying this equation are:-

- i) $k_{js} = 0$ for $|j-s| \neq 1$
- ii) $k_{j,j-1} = j k_{10}$
- iii) $k_{j,j+1} = (j+1)k_{01} = (j+1)k_{10} \exp(-\frac{h\nu}{kT})$
- iv) $k_{js}^a = k_{sj}^a = 0$
- v) $Z_{dj} = Z_0 C P_j N_j N M(D-E_j)$ where Z_0 is the total number of collisions per cc per sec per unit concentrations.

$$\text{vi) } \sum Z_{rj} = \sum k_{rj}[A]^2[x] = [A]^2[x] \sum k_{rj} = K_r [A]^2[x]$$

- vii) $P_j = e^{-(D-E_j)/kU}$ where U is a parameter with dimensions of temperature (see Appendix B for details).

N_j is the fractional number of molecules with vibrational energy E_j , which for a Boltzmann vibrational energy distribution at temperature T_v is given as e^{-E_j/kT_v} and $N = \sum N_j$. $M(D-E_j)$ is the fractional number of collisions with relative kinetic energy along the line of centres greater than or equal to $D-E_j$, thus $M(D-E_j) = e^{-(D-E_j)/kT}$. C is a constant such that, for equal efficiency for dissociation from various vibrational levels, it gives the experimental value of probability P in the overall rate constant expression Eq. (64). For unequal efficiencies, that is $U \neq \infty$, C is put equal to one. K_r is the overall recombination rate coefficient obtained from experiments behind normal shocks.

- viii) $k_{da} = \lambda k_{dm}$, that is the rate constant for atom molecule collisions may be written as a factor times that for molecule-molecule collisions.

3.3.1.1 Significance and Limitations of the assumptions:-

Assumptions i) to iv) have a bearing mainly on the vibrational relaxation since these are concerned with the rate coefficients for transition from one vibra-

brational level to another vibrational level, and this will not alter the total number of molecules and thus will not explicitly affect the dissociation process. However, it will have an implicit effect since the number of molecules in any given level is affected which in turn affects the dissociation rates Zdj .

I Vibrational relaxation:

Assumptions i) to iii) are made in deriving the Landau-Teller equation for vibrational relaxation of a harmonic oscillator from an unexcited to excited state with no dissociation, and they imply, respectively that

i) the rate for multi-quantum level transitions is zero,

ii) the rate coefficient for transition from level j to $j-1$ is j times the rate coefficient for transition from the first excited level to ground level,

iii) the rate coefficient for transition from level j to $j+1$ is $(j+1)$ times the rate coefficient for transition from ground level to the first excited state which in turn is smaller than the rate coefficient for transition from first excited state to ground level by the exponential factor of energy difference between these two levels, namely $h\nu$.

Under these assumptions, the vibrational relaxation time τ_v is related to k_{10} and k_{01} , as (ref. 35);

$$\frac{1}{\tau_v} = k_{10} - k_{01} = k_{10} (1 - e^{-\theta_v/T})$$

As long as one uses experimentally determined τ_v these assumptions should not affect the results unless the form of the vibrational relaxation equation itself is affected by modifications on these assumptions. However, there is the possibility that the vibrational relaxation time obtained from experiments behind normal shocks may not be the same for expansion flows where the relaxation is from a higher to lower excited state as is already discussed in Section 3.2.3. Expressions for k_{10} taking into account anharmonicity and vibrational-vibrational energy transfer were given and discussed by Treanor (Ref. 28). It was shown there that this increases the dissociation rate for flow behind normal shocks compared to those obtained by using the Landau-Teller expression for k_{10} .

Thus, in the present work, τ_v was shortened from its normal shock value to take this factor into account.

The significance of assumption iv) is that the vibrational relaxation by atom exchange is not important. This assumption may be quite appropriate when the number densities of atoms is quite small and when the vibrational excitation is not very high. This is so since this kind of atom exchange is possible when an atom comes within the range of an excited molecule in its outward vibration such that the nearer atoms may form a deexcited molecule.

Thus for the flow behind a normal shock where the overlap region of vibrational relaxation and dissociational reaction is small, this exchange reaction may be considered insignificant. However, for expansion flows of a dissociated gas, where there are sufficient number of atoms, this reaction can be quite important in deexciting the gas. This could have been taken into account by making use of the expression for $k_{j+1 \rightarrow j}$ postulated by Treanor (Ref. 28), namely,

$$k_{js}^a = 0 \quad \text{for } |j-s| \neq 1$$

$$\text{and } k_{j+1 \rightarrow j}^a = (j+1)A_1 \frac{\omega_0}{\omega_j} \frac{T_t}{T_0} \frac{e^{-A_2 M^{1/2} (\omega_j/k)^{4/3} (T_t^{-1/3} - 0.015 M^{1/4})}}{(1 - e^{-\omega_0/k})} \quad (83)$$

Where A_1 , A_2 are constants, M is the reduced mass of the colliding molecules, and $\omega_j = E_{j+1} - E_j$ where E_{j+1} , E_j vibrational energies for levels $j+1$ and j .

Since the introduction of these rates would complicate the calculations, this was not done. The effect of this exchange reaction will be to decrease the vibrational relaxation time. Thus shortening the vibrational relaxation time τ_v from its normal shock undissociated value would be able to take into account this factor on an overall level.

II Dissociational reaction:

The effect of assumptions v) to viii) is on the dissociation reaction.

Assumption vii) gives higher probability or efficiency for dissociation to occur from higher vibrational energy levels whenever U is finite. For $U = \infty$, it gives equal probability for dissociation from all vibrational levels. Though the equal probability assumption is not realistic, it will also be used since it would remove one extra parameter from the problem, and in those cases where the value of U is not important, putting $U = \infty$ will simplify the calculations considerably.

Assumption v) contains a factor $M(D-E_j)$ which is the fractional number of collisions with an energy greater than or equal to $(D-E_j)$. In the most realistic model, one has to take into account in writing this expression, not only the kinetic energy or translational energy of the colliding molecule, but also the vibrational and rotational energies. It was already pointed out in section 3.1.2 that taking these internal energies into consideration will multiply the exponential factor by $(D-E_j/kT_t)^{S/S!}$ where S is 0 for atom-molecule and 1 for molecule-molecule collisions for vibrational and translational equilibrium. Thus

$$M(D-E_j) = (D-E_j/kT_t)^{S/S!} e^{-(D-E_j)/kT_t}$$

for vibrational and translational equilibrium and taking account of all energies.

With this expression for $M(D-E_j)$, the coupling factor will be modified as shown in Appendix B and will complicate the calculations. Thus for simplicity the contributions of internal energies are neglected, giving

$$M(D-E_j) = e^{-(D-E_j)/kT}$$

Assumption vi) means that the recombination rate coefficient is not affected by the vibrational nonequilibrium. This is reasonable since recombination is achieved as a result of collision between two atoms and a third body and, in the model where only the translational energies are taken into account, it does not matter whether the third body, if it is a molecule, is in vibrational equilibrium or not. However, if one takes into account the vibrational and rotational energies also, then the k_{rj} for a molecule as a third body should be modified, while for an atom as a third body no changes are required.

Assumption viii) means that the dissociation rates with molecules or atoms as second bodies are different. This seems to have been borne out from the experimental results of Byron (Ref. 33). The value of λ is $\frac{35T}{\theta}$ as derived in Appendix B from Byron's experiments.

3.3.2 Dissociational rate equation:-

Under the above assumptions the rate equation for dissociation may be written as (See Appendix B for details)

$$\frac{D\alpha}{Dt} = \frac{k_r p^2 (1-\alpha + 2\lambda\alpha)}{m_a^2} \alpha^2 \left[V K_C \frac{m_a}{2p} \cdot \frac{(1-\alpha)}{\alpha^2} \right] = \psi [VL - 1] \quad (84)$$

where α is atomic mass fraction,
 k_r is the recombination rate constant obtained from normal shock experiments,
 p is the density,
 m_a is the mass of atoms per unit mole
 $K_C = k_{eq}/k_r$ is the equilibrium constant given by Eq. (B85)
 $V = \frac{Q(T_e) Q(T_f)}{Q(T) Q(U)}$ is the coupling factor due to vibrational nonequilibrium such that $k_d = V k_{d eq}$.

Q 's are vibrational partition functions with appropriate T ,

$$\frac{1}{T_f} = \frac{1}{T_v} - \frac{1}{T_k} - \frac{1}{U} \quad (85)$$

$$\psi = k_r p^2 (1-\alpha + 2\lambda\alpha) \alpha^2 / m_a^2 \quad (86)$$

$$L = \frac{K_C m_a}{2p} \frac{(1-\alpha)}{\alpha^2} \quad (87)$$

3.3.3 Vibrational relaxation equation:-

The rate equation for the net rate of change of the vibrational energy per unit mass \mathcal{E}_v may be written as (see Appendix B for details)

$$\frac{D\mathcal{E}_v}{Dt} = \frac{\mathcal{E}_\infty - \mathcal{E}_v}{\tau_v} - \frac{(\bar{E} - \mathcal{E}_v)\chi VL}{(1-\alpha)} + \frac{(\bar{G} - \mathcal{E}_v)\chi}{(1-\alpha)}$$

where \mathcal{E}_v is the actual vibrational energy per unit mass
 \mathcal{E}_∞ is the vibrational energy per unit mass calculated at translational temperature T_t
 \bar{E} is the average energy lost per dissociation = $\mathcal{E}(T_f)$
 \bar{G} is the average energy gained per recombination = $\mathcal{E}(-U)$
 \mathcal{E} 's may be written as = $\sum E_j \exp(E_j/kT)/Q(T)$ with the appropriate temperature T .
 τ_v vibrational relaxation time

4. BASIC EQUATIONS OF MOTION

The basic equations of motion are:

$$\text{Mass: } \frac{D\rho}{Dt} + \rho \operatorname{div} \vec{q} = 0 \quad (88)$$

$$\text{Momentum: } \frac{D\vec{q}}{Dt} + \frac{1}{\rho} \operatorname{grad} p = 0 \quad (89)$$

$$\text{Energy: } \frac{Dh}{Dt} - \frac{1}{\rho} \frac{Dp}{Dt} = 0 \quad (90)$$

$$\text{State: } p = \rho R T_t (1 + \alpha) \quad (91)$$

$$\text{Enthalpy: } h = \frac{7+3\alpha}{2} R T_t + R(1-\alpha)\mathcal{E}_v + R\theta_0 = h(\alpha, T_t, \theta_0) \quad (92)$$

$$\text{Rate: dissociational } \frac{D\alpha}{Dt} = \psi(VL - 1) \quad (93)$$

$$\text{vibrational } \frac{D\mathcal{E}}{Dt} = \frac{\mathcal{E}_\infty - \mathcal{E}_v}{\tau_v} - \frac{\chi VL(\bar{E} - \mathcal{E}_v)}{(1-\alpha)} + \frac{\chi(\bar{G} - \mathcal{E}_v)}{(1-\alpha)} \quad (94)$$

Where p , ρ , \vec{q} , α , T_t , \mathcal{E}_v , h are pressure, density, velocity, atomic mass fraction, translational temperature, specific vibrational energy and specific enthalpy respectively. The equation for specific entropy variation and the expression for specific entropy are given in Eqs. (A36), (A18). ψ , V , L , \bar{E} , \bar{G} , τ_v are defined in Section 3.3. The differential operator is $\frac{D}{Dt} = \frac{\partial}{\partial t} + \vec{q} \cdot \operatorname{grad}$. For steady, one-dimensional flows $\frac{D}{Dt} = \vec{q} \frac{d}{dx}$ where \vec{q} is the speed and x is the coordinate in the flow direction. For steady, adiabatic flows, the energy and momentum equations give along a streamline,

$$h + \frac{\vec{q}^2}{2} = h_0 = \text{constant} \quad (95)$$

For flow from a reservoir, h_0 is the same on all streamlines.

4.1 Dissociational models:-

Eqs. (88) to (94) are the equations to be solved for the problem of simultaneous vibrational and dissociational nonequilibrium of a pure dissociated diatomic gas. It would be of interest to compare the form of these equations with those for the various dissociation models referred to in the introduction.

Namely:

- i) Ideal or Lighthill dissociating gas model.
- ii) Vibrational equilibrium - dissociational nonequilibrium model.
- iii) Uncoupled but simultaneous vibrational and dissociational nonequilibrium model.
- iv) Coupled vibrational and dissociational nonequilibrium model with (a) equal efficiency of dissociation from all vibrational energy levels; called the non-preferential model, (b) higher efficiency or preference from higher vibrational energy levels, called the preferential model.

Now these various dissociation models will affect the form of the rate equations (93) and (94) for vibration and dissociation and the enthalpy expression h in Eq. (92) but will not affect the form of the equations of mass, momentum and energy, that is Eqs. (88) - (90), and the state equation (91). The dissociational models fall into two distinct types, namely those which assume vibrational equilibrium, that is cases (i) and (ii); and those which assume vibrational nonequilibrium i. e. cases (iii) and (iv).

4.1.1 Vibrational nonequilibrium models:-

4.1.1.1 Coupled Preferential dissociation model:-

For simultaneous nonequilibrium in vibration and dissociation, the coupled preferential model is the most realistic postulated here provided one can prescribe the correct value of the parameter U .

It should be recalled however that it has been assumed that the vibrational nonequilibrium process can be characterized by a vibrational temperature T_v - which differs from the translational temperature T_t , and that this assumption implies a Boltzmann distribution of vibrational energy. For the flow region behind a normal shock advancing into an undissociated gas Treanor (Ref. 28) has shown that a more appropriate model would be that of vibrational relaxation from a steady-state distribution which is non-Boltzmann. This is so since initially only dissociation occurs since there are no atoms to recombine, thus depleting the upper vibrational energy levels and thus producing a non-Boltzmann distribution. However, Treanor points out that as soon as the recombination gains importance this unbalance is removed and a Boltzmann distribution in vibration is restored. Thus for the expansion flow of a dissociated

gas which is initially in thermal and chemical equilibrium, the recombination process is as important as dissociation and thus the model of vibrational relaxation from a Boltzmann distribution in vibration appears to be quite good. For this same reason, prescription of U as a solution of Eq. (B65), namely

$$\frac{e^{\theta_v/2U}}{Q(-U)} = \frac{Z_0}{2T^n Q(T_t)} \quad (\text{B65})$$

for expansion flows is quite realistic. This relation is obtained by equating k_d from the present model for $T_t = T_v$ with the experimental k_d measured under vibrational equilibrium conditions.

However, as the solution of this equation for U is involved, a value of $U = \frac{\theta_v}{6}$ was used following the suggestion of Treanor and Marrone (Ref. 21). This value of U gives higher efficiency or preference for dissociation from higher vibrational energy levels as

$$p_j = e^{-(D-E_j)/kU} = e^{-6(1 - \frac{\theta_{v_i}}{\theta_v})}$$

which is plotted in Fig. 1.

This model is called coupled since the effect of vibrational nonequilibrium is taken into account in the dissociational rate equation (93) through the coupling factor V

$$V = \frac{Q(T_t)}{Q(T_v)} \quad \frac{Q(T_f)}{Q(-U)}$$

where the dependence on T_v and U is clearly seen. It can be shown that $V \geq 1$ in the expansion flow since $T_v \geq T_t$. The implication of this may be better appreciated by recalling that by definition, $V = k_d/k_{deq}$, so that $V \geq 1$ implies that the nonequilibrium dissociation rate is greater than or equal to that for vibrational equilibrium. Physically the observation $T_v > T_t$ means that there is more energy in vibration than when $T_v = T_t$ so that the molecules are more easily dissociated. Hence $k_d \geq k_{deq}$. Also by substituting for k_{dvibeq} ~~eq~~ from Eq. (B63) and for V , one obtains for the dissociation rate constant under vibrational nonequilibrium

$$\begin{aligned} k_d &= V \cdot k_{dvibeq} \\ &= \frac{Q(T_t)}{Q(T_v)} \cdot \frac{Q(T_f)}{Q(-U)} e^{-\theta_v/2U} e^{-\theta_v/T_t} \frac{Q(-U)}{Q(T_t)} \\ &= \frac{e^{-\theta_v/2U} Q(T_f)}{Q(T_v)} e^{-\theta_v/T_f} \end{aligned}$$

$$= k_d (T_t, T_v, U)$$

thus showing that k_d is not only a function of T_t and U as in vibrational equilibrium, but also a function of T_v .

The effect of dissociational nonequilibrium on vibrational nonequilibrium is taken into account by the last two terms of Eq. (94) which are the vibrational energies lost due to dissociation and gained due to recombination respectively.

4. 1. 1. 2 Coupled nonpreferential model:-

In this model it is assumed that dissociation occurs with equal efficiency or with no preference from the various vibrational levels. From the form of the efficiency factor

$$P_j = e^{-(D-E_j)/kU}$$

it will be seen that putting $U = \infty$ makes $P_j=1$ for all j . Thus the model with $U = \infty$ is called the non-preferential coupled dissociation model.

The coupling factor V simplifies in this case to

$$V = \frac{Q(T_t)}{Q(T_v)} \cdot \frac{Q(T_m)}{N}$$

where $\frac{1}{T_m} = \frac{1}{T_v} - \frac{1}{T_t}$ and N is the total number of vibrational levels. This is so since

$$\frac{1}{T_f} = \frac{1}{T_v} - \frac{1}{T_t} - \frac{1}{U} = \frac{1}{T_v} - \frac{1}{T_t} = \frac{1}{T_m}$$

$$\text{and } Q(-U) = \sum_j e^{E_j/kU} = \sum_j 1 = N$$

The average energies lost in dissociation and recombination \bar{E} and \bar{G} , simplify to

$$\bar{E} = \frac{\sum E_j e^{-E_j/kT_f}}{\sum e^{-E_j/kT_f}} = \frac{\sum E_j e^{-E_j/kT_m}}{\sum e^{-E_j/kT_m}} = \varepsilon(T_m)$$

$$\bar{G} = \frac{\sum E_j e^{E_j/kU}}{\sum e^{E_j/kU}} = \frac{\sum E_j}{N}$$

In this case also $V \geq 1$ since $T_v \geq T_t$. But it is difficult to say if V in the nonpreferential case will be greater or less than V in the preferential case. However, one can say that \bar{E} and \bar{G} , for the nonpreferential model will be less than those for the preferential model.

4. 1. 1. 3 Uncoupled Model:-

In the uncoupled model, it is assumed that vibrational nonequilibrium has no effect on dissociation and vice versa. In other words V is taken equal to unity and the net effect of the last two terms in the vibrational rate equation (94) is considered to be negligible. This will be reasonably true only for vibration and dissociation very near equilibrium. Then the number of dissociations is roughly equal to the number of recombinations and so is the average energies lost or gained. However, where vibration and dissociation are sufficiently out of equilibrium such that one of them predominates this will be a very poor approximation.

The rate equation for the uncoupled model will thus be

$$\frac{D\alpha}{Dt} = \psi (L - 1)$$

$$\frac{D\mathcal{E}_v}{Dt} = \frac{\mathcal{E}_\infty - \mathcal{E}_v}{\tau_v}$$

4. 1. 1. 4 Limits on the coupling factor V :-

In the normal shock case where T_v is always less than T_t , V always lies between 0 and 1.

However for the expansion case T_v is greater than T_t and may in course of time freeze thus increasing the difference between them. Thus to start with $V \approx 1$ since $T_t \approx T_v$. If the proper relation between T_t and U given by Eq. (B65) is used, then

$$\begin{aligned} V &= \frac{Q(T_t)}{Q(T_v)} \cdot \frac{Q(T_f)}{Q(-U)} = \frac{Q(T_t)}{Q(T_v)} \cdot \frac{Q(T_f) Z_0}{a T_t^n Q(T_t) e^{a/U}} \\ &= \frac{Z_0}{a} T_t^{-n} e^{-a/U} \frac{Q(T_f)}{Q(T_v)} \end{aligned}$$

where n is positive. As T_t goes on decreasing and T_v remains constant, it would appear that V should ultimately tend to zero after reaching a maximum. This is necessary to be consistent to be with the concept of freezing. This situation should be the same for preferential or non-preferential models.

4. 1. 2 Vibrational equilibrium models:-

For vibrational equilibrium \mathcal{E}_v drops out as an independent variable since $T_t = T_v$ and $\mathcal{E}_\infty = \mathcal{E}_v$ and thus, the vibrational rate equation

$$\frac{D\mathcal{E}_v}{Dt} = \frac{\mathcal{E}_\infty - \mathcal{E}_v}{\tau_v}$$

would simply be a function of T_t . This situation occurs in the limit $\tau_v \rightarrow 0$

The ideal dissociating gas case is a further simplification of this model and is discussed in great detail in Ref. 5.

4.2 One dimensional Flow:-

For one dimensional, steady flow through a nozzle, the continuity equation is replaced by

$$\rho g A = \text{constant} = \dot{m}_{re} \quad (96)$$

where A is the area of the nozzle at a given section x. The determination of this constant \dot{m}_{re} is discussed below in Section 4.2.3. The solution of this flow problem may be conveniently carried out by a system of three algebraic equations, (Eqs. (96), (95), (91), for mass, enthalpy and state), and three coupled ordinary differential equations for T_t , E_v , α . The equations for E_v and α are immediately obtained by replacing the operator,

$$\frac{D}{Dt} \text{ by } g \frac{d}{dx} \text{ to obtain}$$

$$\frac{d\alpha}{dx} = \frac{\psi}{g} (VL - 1) \quad (97)$$

$$\frac{dE_v}{dx} = \frac{1}{g} \frac{E_{\infty} - E_v}{\tau_v} - \frac{\psi VL (\bar{E} - E_v)}{(1 - \alpha)} + \frac{\psi (\bar{G} - E_v)}{(1 - \alpha)} \quad (98)$$

The derivation of the equation for T_t is straightforward. The mass, momentum, energy equations are

$$\frac{1}{\rho} \frac{d\rho}{dx} + \frac{1}{g} \frac{dg}{dx} + \frac{1}{A} \frac{dA}{dx} = 0 \quad (99)$$

$$g \frac{dg}{dx} + \frac{1}{\rho} \frac{d\rho}{dx} = 0 \quad (100)$$

$$\frac{dh}{dx} - \frac{1}{\rho} \frac{d\rho}{dx} = h_{T_t} \frac{dT_t}{dx} + h_{E_v} \frac{dE_v}{dx} + h_{\alpha} \frac{d\alpha}{dx} - \frac{1}{\rho} \frac{d\rho}{dx} = 0 \quad (101)$$

From state equation

$$\frac{1}{\rho} \frac{d\rho}{dx} = \frac{1}{\rho} \frac{d\rho}{dx} + \frac{1}{T_t} \frac{dT_t}{dx} + \frac{1}{1 + \alpha} \frac{d\alpha}{dx} \quad (102)$$

From these four equations $\frac{d\rho}{dx}$, $\frac{dT_t}{dx}$, $\frac{dE_v}{dx}$, $\frac{d\alpha}{dx}$ can be eliminated leading to the equation for $\frac{dT_t}{dx}$ as.

$$\frac{dT_t}{dx} = \frac{g^2}{(1-M_f^2)(\frac{7+3\alpha}{2})} \left\{ \frac{1}{A} \frac{dA}{dx} - \frac{1}{1+\alpha} \frac{d\alpha}{dx} + \left(\frac{1}{T(1+\alpha)} - \frac{1}{g^2} \right) \left[\left(\frac{3}{2} T_t - \epsilon_v + \theta_b \right) \frac{d\alpha}{dx} + (1-\alpha) \frac{d\epsilon_v}{dx} \right] \right\} \quad (103)$$

where M_f is the frozen Mach number given by

$$M_f^2 = \frac{g^2}{a_f^2} \quad (104)$$

and a_f^2 is the frozen speed of sound given by (see Ref. 5)

$$a_f^2 = \frac{7+3\alpha}{5+\alpha} R T_t (1+\alpha) \quad (105)$$

The solution of the flow problem is completely given by solving Eqs. (91), (95), (96), (97), (98), (103).

4.2.1 Effect of the various dissociation models on quasi-one dimensional Flow equations:-

It is already shown in Section 4.1 how the various dissociation models modify the rate equations for vibration and dissociation. For one dimensional flow, the right hand side of Eqs. (97), (98) will be simplified in the same way. In addition, for the vibrational equilibrium model, in the expression for the enthalpy given by Eq. (92), the vibrational contribution ϵ_v will no longer be an independent variable and thus in Eq. (101), the term $\frac{d\epsilon_v}{dx}$ may be written as $\frac{d\epsilon_v}{dT_t} \cdot \frac{dT_t}{dx}$ which simplifies Eq. (103) to

$$\frac{dT_t}{dx} = \frac{g^2}{(1-\bar{M}_f^2)(\frac{7+3\alpha}{2} + \frac{d\epsilon_v}{dT_t})} \left\{ \frac{1}{A} \frac{dA}{dx} - \frac{1}{1+\alpha} \frac{d\alpha}{dx} + \left(\frac{1}{T(1+\alpha)} - \frac{1}{g^2} \right) \left(\frac{3}{2} T_t - \epsilon_v + \theta_b \right) \frac{d\alpha}{dx} \right\}$$

where \bar{M}_f^2 is the partially frozen Mach number referred to the partially frozen sound speed \bar{a}_f^2 , i.e. $\bar{M}_f^2 = \frac{g^2}{\bar{a}_f^2}$

$$\bar{a}_f^2 = \frac{\frac{7+3\alpha}{2} + (1-\alpha) \frac{d\epsilon_v}{dT_t}}{\frac{5+\alpha}{2} + (1-\alpha) \frac{d\epsilon_v}{dT_t}} R T_t (1+\alpha)$$

For vibrational nonequilibrium model, Eq. (103) is not changed in any way. i.e. it is only the frozen Mach number M_f that enters in Eq. (103) and the $\frac{d\epsilon_v}{dx}$ term remains inside the bracket on RHS of Eq. (103).

4.2.2 Isentropic limiting flows:-

One can further consider some limiting flows which are isentropic and which can be calculated as the solution of a system of algebraic equations. These are:

- i) Vibration and dissociation frozen, or fully frozen case,
- ii) Vibration in equilibrium with translation while dissociation is frozen, or partially frozen case,
- iii) Vibration and dissociation in equilibrium or full equilibrium case,
- iv) Vibration frozen while dissociation is in equilibrium, or partially frozen case.

In all these cases it can be shown that the flow is isentropic. It is doubtful if case (iv) is ever realized for real flows. Thus only cases (i) to (iii) will be considered. In all these cases, whether vibration is frozen or in equilibrium it drops out as an additional variable since for frozen vibration T_v is constant while for vibrational equilibrium $T_t = T_v$. When dissociation is also frozen α also drops out as a variable since it is constant while for dissociational equilibrium, one has the additional relation between α , p , T_t given by (A34) in Appendix A. Also since the flow is isentropic one can use the entropy equation given by (A18) in Appendix A as a further relation between α , T_t and T_v . This entropy equation is rederived as an integral of the differential flow relations for cases (ii) and (iii) in Appendix C. Thus these limiting cases can be calculated as a solution of the following set of algebraic equations:-

$$\text{Mass } \rho g A = \text{constant} = \dot{m}_c$$

$$\text{energy } h + \frac{g^2}{2} = h_0 = \text{constant}$$

$$\text{state } p = p R T_t (1 + \alpha)$$

$$\text{enthalpy } h = \frac{7+3\alpha}{2} R T_t + (1-\alpha) R E_v + R \alpha \theta_D$$

$$\text{dissociation equilibrium } \frac{\alpha e^2}{1-\alpha e} = \frac{2 p_D}{p} \left(\frac{T_t}{\theta_D} \right)^{\frac{1}{2}} (1 - e^{-\theta_v/T_t}) e^{-\theta_D/T_t}$$

$$\text{entropy } \frac{S-S_r}{R} = \frac{3\alpha}{2} + \frac{(1-\alpha) E_v}{T_t} + (1+\alpha) \frac{\theta_D}{T_t} + 2 \log \left[\frac{\alpha T_t}{(1-\alpha) T_t (1 - e^{-\theta_v/T_t})} \right] \\ + (1+\alpha) \log \left[\frac{2 p_D}{p} \left(\frac{T_t}{\theta_D} \right)^{\frac{1}{2}} (1 - e^{-\theta_v/T_t}) e^{-\theta_D/T_t} \frac{(1-\alpha)}{2} \right] = \text{Constant}$$

For dissociational equilibrium, the last term in the entropy equation is zero since the expression logarithmic term becomes zero. This may be seen from the equilibrium relation for α .

It may be noted that this relation derived in Ref. 8 is in error due to the omission of the $(1-\alpha) E_v / T_t$ for vibrational and dissociational equilibrium.

Thus for dissociational equilibrium,

$$\frac{S - S_r}{R} = \frac{3\alpha}{2} + \frac{(1-\alpha) \epsilon_v}{T_r} + (1+\alpha) \frac{\theta_v}{T_r} + 2 \log \left[\frac{\alpha T_t}{(1-\alpha) T_r (1 - e^{-\theta_v/T_r})} \right] = \text{Constant} = \frac{S_0}{R}$$

For frozen dissociation, all terms containing α only and constants like ρ_D , θ_v , etc. can be incorporated into S_r , thus giving the relation between p and T_t as

$$\frac{S - S_r'}{R} = \frac{5+\alpha}{2} \log T_t + (1-\alpha) \left[\frac{\epsilon_v}{T_r} - \log(1 - e^{-\theta_v/T_r}) \right] - (1+\alpha) \log p = \text{Constant} = \frac{S_0}{R}$$

where $S_r' = S_r + R \left[\frac{3\alpha}{2} - 2\alpha \log \alpha - (1-\alpha) \log(1-\alpha) - (1+\alpha) \log \frac{\rho_D}{\theta_v^{1/2}} - 2 \log T_r \right]$

The constants $\frac{S_0}{R}$ can be evaluated for the reservoir conditions. These entropy equations are the same as those derived in Appendix C starting from differential flow relations.

In order to complete these equations one has to determine the critical mass flow M_c . For these limiting flows another algebraic equation can be obtained by requiring that at $\frac{dA}{dx} = 0$, the Mach number (referred to frozen, partially frozen or equilibrium sound speeds discussed in Ref. 5 in the respective cases) be unity. This is so since in all these cases Eq. (103) can be shown to simplify to

$$\frac{dT_t}{dx} = \frac{\rho^2 \frac{1}{A} \frac{dA}{dx}}{(1-M^2) h T_t}$$

Where M is the appropriate Mach number. The $\frac{d\epsilon_v}{dx}$, $\frac{d\alpha}{dx}$ terms in Eq. (103) either drop out (for the frozen cases) or are incorporated in $\frac{dT_t}{dx}$ term (for equilibrium α , ϵ_v are functions of T_t). Thus for $M=1$, if the derivative $\frac{dT_t}{dx}$ is to be finite, $\frac{dA}{dx}$ should be zero, that is when $\frac{dA}{dx} = 0$ (at the throat) the Mach number is unity.

This algebraic equation is derived in Appendix C for partially frozen and equilibrium flows. This equation along with all the other equations except the mass continuity equation determines the critical conditions from which the critical mass flow is obtained.

4.2.3 Determination of mass flow under nonequilibrium conditions:-

The determination of the critical mass flow is not as straightforward as in the limiting flows. The location of the point where the Mach number becomes unity cannot be a priori determined as in the limiting flows. For, from Eq. (103),

$$\frac{dT_t}{dx} = \frac{\rho^2}{(1-M^2) \frac{1+\alpha}{2}} \left\{ \frac{1}{A} \frac{dA}{dx} - \frac{1}{1+\alpha} \frac{d\alpha}{dx} + \left(\frac{1}{T(1+\alpha)} - \frac{1}{\rho^2} \right) \left[\frac{3}{2} T - \epsilon_v + \theta_D \right] \frac{dT_t}{dx} + (1-\alpha) \frac{d\epsilon_v}{dx} \right\}$$

one can only say that when $M_f = 1$, the expression within brackets should be zero if dT_e/dx is to remain finite. Since this expression contains $dE_v/dx, d\alpha/dx$ which themselves depend on the past history of the flow in the subsonic portion of the nozzle, the point where $M_f = 1$ occurs can only be determined by obtaining a complete solution to the problem. However, it can be shown by a simple argument that the point for which $M_f = 1$ occurs downstream of the throat. We can define a local equilibrium Mach number by using the equilibrium sound speed calculated using local values of α and T determined for the nonequilibrium flow. This local equilibrium Mach number is unity at the geometrical throat. (Ref. 41).

Since the frozen Mach number is less than the equilibrium Mach number, the point for which $M_f = 1$ must be downstream of the throat.

Thus the nonequilibrium critical mass flow M_{xe} has to be determined by an iteration scheme which uses the mass flows for fully frozen and equilibrium cases as limits. This iteration is done by first choosing for M_{xe} a value between m_f (frozen) and m_e (equilibrium) and then calculating the nonequilibrium flow up to some point downstream of the geometric throat. If the initial value chosen is less than the critical value, then M_f reaches a maximum value which is less than unity and then begins to decrease; if this initial value is greater than the critical value, then M_f reaches a value greater than or near unity and integration no longer can proceed forward. In the former case, a new larger value for M_{xe} is chosen and in the latter case, a new smaller value is chosen; and the calculations continued until these two limits coincide. This procedure gives the nonequilibrium critical mass flow and the point where $M_f = 1$.

Now it is not possible to carry a numerical computation through the frozen sonic point in any nozzle flow calculation. This applies to perfect gas flows, as well as nonequilibrium flows. The reason is that at the critical point quantities like dT_e/dx approach the form $0/0$. One simple way of surmounting this problem, and it is the one that is used here, is to apply small discontinuous jumps to all variables to carry them through this point. This is further discussed in Section 5 and Appendix D.

4.2.4 Initial conditions for starting nonequilibrium flow calculations:-

The implication of the limiting flows on the rate equations is as follows:

For instantaneous equilibrium of vibration and dissociation with local conditions, the Eqs. (97) and (98) simplify to

and

$$\frac{d\alpha}{dx} = \frac{\psi}{f} (VL - 1) = \frac{\psi}{f} \left[\frac{K_c M_a}{2P} \frac{(1 - \alpha_e)}{\alpha_e^2} - 1 \right] = \frac{\psi}{f} \times 0$$

$$\frac{dE_v}{dx} = \frac{E_\infty - E_v}{f \tau_v} - \frac{(\bar{G} - E_v) \psi (VL - 1)}{f (1 - \alpha)} = \frac{0}{f \tau_v}$$

but $\frac{d\alpha}{dx}$ and $\frac{dE_v}{dx}$ are not zero in equilibrium flows. Thus for $\frac{d\alpha}{dx}$ and $\frac{dE_v}{dx}$ to remain finite, $\frac{\psi}{q}$ and $\frac{1}{q\tau_v}$ should tend to zero. However, ψ and τ_v are always finite since they involve only the rates of reaction and of relaxation.

$$\text{Thus } \frac{\psi}{q} \longrightarrow 0 \text{ and } \frac{1}{q\tau_v} \longrightarrow 0$$

can happen only for $q \rightarrow 0$. However, for any q different from zero, these conditions are realized only by making $\psi \rightarrow \infty$ and $\tau_v \rightarrow 0$. Thus the instantaneous equilibrium assumption for a flowing gas implies infinite rates such that $\psi \rightarrow \infty$ and $\tau_v \rightarrow 0$.

Similarly for the frozen limit,

$$\begin{aligned} \frac{d\alpha}{dx} &= 0 = -\frac{\psi}{q}(VL-1) \\ \frac{dE_v}{dx} &= 0 = \frac{E_\infty - E_v}{q\tau_v} - \frac{\psi VL(\bar{E} - E_v)}{q(1-\alpha)} + \frac{\psi(\bar{G} - E_v)}{q(1-\alpha)} \end{aligned}$$

The quantities $VL-1$, $E_\infty - E_v$, $\frac{VL(\bar{E} - E_v)}{1-\alpha}$, $\frac{\bar{G} - E_v}{q(1-\alpha)}$ all differ from zero.

Thus $\frac{d\alpha}{dx} = \frac{dE_v}{dx} = 0$ can be realized only by making

$$\frac{\psi}{q} \longrightarrow 0 \text{ and } \frac{1}{q\tau_v} \longrightarrow 0$$

Again ψ and τ_v being finite in reality, this limit is possible only for $q \rightarrow \infty$ that is for infinitely accelerating flow. However for any finite q , one may interpret these conditions to mean $\psi, \frac{1}{\tau_v} \rightarrow 0$, in other words zero reaction and relaxation rates.

From this one may conclude that starting from the reservoir, the flow will begin to fall out of equilibrium slowly as q/ψ and $q\tau_v$ become appreciable (as q increases slowly from zero in the reservoir) and will begin to freeze as soon as q becomes large enough for ψ/q and $1/q\tau_v$ to be very near zero.

Thus the transition from equilibrium to nonequilibrium and nonequilibrium to frozen is nonuniform since in the first case ψ and $\frac{1}{\tau_v}$ change from infinite values to finite values, while in the second case, they change from finite values to zero. This transition from equilibrium to nonequilibrium is a problem which one encounters in the calculation of nonequilibrium flows. For finite rates, starting nonequilibrium calculations from equilibrium initial values of α , T_v , T_t yield

$$\left[\frac{d\alpha}{dx} \right]_{\text{neg}} = \left[\frac{dE_v}{dx} \right]_{\text{neg}} = 0 \neq \left[\frac{d\alpha}{dx} \right]_{\text{eq}}, \left[\frac{dE_v}{dx} \right]_{\text{eq}} \text{ And } \left[\frac{dT_t}{dx} \right]_{\text{eq}} = \left[\frac{\frac{\partial A}{\partial x}}{h_{T_0}(1-M_e^2)} \right]_{\text{eq}} \neq \left(\frac{dT_t}{dx} \right)_{\text{neg}} = \text{Eq. (104)}$$

thus giving a discontinuity in the derivatives while the variables themselves are continuous. When the flow is very near equilibrium, the derivatives rapidly reach their true values as is seen in Figs. 4c, 4d. This procedure was suggested in reference 14 and is adopted in the present work.

5. SPECIFIC CALCULATIONS

With the thermodynamic and collisional models discussed in the earlier sections, two sets of calculations were made for the flow of pure dissociated oxygen through nozzles.

5.1 Aims of the Calculations:-

I. The first set of calculations were made with the following aims:

i) To find out how much nonequilibrium calculations started at a point downstream of the geometric throat, where the frozen Mach number M_f is slightly greater than one, differ from nonequilibrium calculations started from a point well upstream of the geometric throat.

ii) To find out if, when the gas is highly dissociated (for example, atomic mass fraction $\alpha = 0.95$) so that the vibrational energy is very small when compared with the energy in dissociation, calculations made under the assumption of vibrational equilibrium will in any way affect the atomic mass fraction.

iii) To study the effect of the parameter U , that is the efficiency factor for dissociation from various vibrational energy levels.

For these calculations, with $T_0 = 5900^\circ\text{K}$, two values of p_0 , 82 atm and 9.4 atm were chosen. For the purposes of this study, an axisymmetric hyperbolic nozzle with the area ratio variation given by

$$\frac{A}{A^*} = 1 + \left(\frac{x}{l}\right)^2 \quad (106)$$

was chosen, since calculations with vibrational equilibrium are available. Two values of U were chosen, namely $U = \infty$ and $U = \theta_D/6$. The value $U = \infty$ corresponds to equal efficiency of dissociation from all the vibrational levels, while $U = \theta_D/6$ gives the efficiency variation from level to level as

$$p_j = e^{-(D-E_j)/kU} = e^{-6(1-\theta_{vj}/\theta_D)} \quad (107)$$

The calculations for $U = \infty$ and $U = \theta_D/6$ correspond to the coupled nonpreferential and preferential dissociation models respectively, where

$$\theta_{vj} = E_j/k$$

II. The second set of calculations were carried out for experimental conditions obtained in the UTIAS 11" x 15" Hypersonic shock tunnel for pure dissociated oxygen flow given in Table I. A sketch of the tunnel is given in Fig. 2 and the area ratio variation of the primary nozzle is given in Fig. 3. The nozzle geometry was divided into five sections and a fifth order polynomial fit made for each section. The coefficients are given in Table II. They were chosen so that the gradient dA/dx as well as A was continuous at the junction points.

The flow through the corner expansion fan of the deflection plate and the terminal wedge nozzle were found to be frozen, thus allowing the use of simple isentropic relations based on the frozen values of T_v and α at the end of the primary nozzle. Boundary layer corrections were applied in the primary nozzle under the frozen boundary layer approximation using the formula for boundary layer displacement thickness given by Burke and Bird (Ref. 39) for turbulent flows, namely

$$\frac{\delta^*}{x} = 0.49 \left(p_r \rho_e x / \mu_r \right)^{-0.3} \quad (108)$$

where p_r and μ_r are evaluated at a reference enthalpy h_r given by

$$h_r = 0.22 (h_o - h_e) + 0.5 (h_w + h_e) \quad (109)$$

where subscripts r, o, e, w refer to reference, stagnation, edge of boundary layer and nozzle wall values. The nozzle wall was taken to be at room temperature. The viscosity of pure dissociated oxygen is calculated from the Sutherland model as given in Ref. 40, namely,

$$\mu_{O_2} = 1.70 \times 10^{-4} T^{2.5} (1 + 138/T)^{-1} \text{ gm/cm sec} \quad (110)$$

The aim of these calculations was:

i) to find out the effect of variation in the vibrational relaxation times on the flow properties;

ii) to consider the effects of slight variation in p_o , T_o values, keeping one of them approximately constant. This was necessary because the stagnation pressure behind the reflected shock in the reservoir upstream of the primary nozzle showed variations during the test period due to over-tailoring, making it difficult to give a proper T_o from the measured p_o and incident shock Mach number. This p_o was always less than that predicted

TABLE I

Experimental conditions for the pure dissociated oxygen flow in the 11" x 15"
UTIAS Hypersonic Shock Tunnel.

Terminal nozzle entrance 11" x 0.4"

p_1 (mmHg)	M_s	$P_{o\text{ Theo.}}$ (atm)	$T_{o\text{ Theo}}$ (°K)	$P_{o1\text{ Exptl}}$ (atm)	$P_{o2\text{ Exptl}}$ (atm)	T_{o2} (°K)
25	8.03	23.13	4040	19.05	20.82	3960
25	9.62	40.82	4630	34.01	39.46	4600
10	9.63	16.67	4350	12.93	14.18	4210
10	11.00	24.49	4800	19.73	22.10	4750
-	-	22.45	4600	-	-	-

p_1 = initial pressure in the channel

M_s = shock Mach number

$P_{o\text{ Theo.}}$, $T_{o\text{ Theo}}$ = calculated by equilibrium theory from p_1 and M_s

$P_{o1\text{ exptl}}$, $P_{o2\text{ exptl}}$ = two plateau values experimentally observed
due to overtailing

T_{o2} = calculated for $P_{o2\text{ exptl}}$ from $T_{o\text{ Theo.}}$ and $P_{o\text{ Theo.}}$ under
the assumption of isentropic compression.

See Footnote

Footnote:

Due to reflected shock boundary layer interaction, the conditions immediately behind the shock are different from those given by theory for given p_1 and M_s . Also, whenever there is perfect tailoring the pressure trace for the pressure behind the reflected shock should remain constant until the reflected head or tail of the expansion wave arrives at the nozzle end of the shock tube. For combustion runs, the range of tailored shock Mach numbers is limited for given driver and driven gas combinations forcing one to use over-tailored conditions to obtain higher shock Mach numbers. Under such conditions, one observes a pressure rise due to the compression waves produced by the reflected shock-contact surface interaction. Under the assumption that behind the reflected shock all processes are isentropic, one can calculate T_{o1} , T_{o2} from $P_{o\text{ Theo}}$ and experimental P_{o1} and P_{o2} .

TABLE II

Coefficients in the polynomial fits for the area ratio variation of the UTIAS
HST primary nozzle:

range of χ (inches)	a_0	a_1	a_2	a_3	a_4	a_5
$-1.2 \leq \chi \leq -0.8$	-49.84334	-158.4928	-156.5498	-55.48355	0	0
$-0.8 \leq \chi \leq -0.4$	-5.399903	-36.54116	-59.99915	-38.54122	0	0
$-0.4 \leq \chi \leq -0.11$	1.0	0.4166667	-21.61491	-14.32370	0	0
$-0.11 \leq \chi \leq 1.2$	1.0	0.4166667	0	0	0	0
$1.2 \leq \chi \leq 3.0$	0.70009936	0.55533466	0.11590198	0.03854181	0	0
$3.0 \leq \chi \leq 5.4$	-6.1320435	0.5971668	-0.9679386	0.09266074	0	0
$5.4 \leq \chi \leq 31.5$	-14.637513	6.4113094	-0.4268819	0.02090338 -0.0005340	0.0000515	

$$\frac{A}{A^*} = a_0 + a_1 \chi + a_2 \chi^2 + a_3 \chi^3 + a_4 \chi^4 + a_5 \chi^5$$

$$A^* = 0.36''$$

on the basis of initial channel pressure and shock Mach number.

iii) finally, to give the flow parameters in the test section, in particular the atomic mass fraction so that comparisons can be made with some experimental measurements of atom concentration currently being made in the UTIAS hypersonic shock tunnel (Ref. 45).

The results of these calculations are plotted in Figs. 4 to 10. Fig. 11 gives a comparison between theory and experiment of test section static pressure. Table IV gives the comparative values of T_t , T_v , α , ρ and P at the end of the primary nozzle, after the deflection plate and in the test section. The effects of variation of the vibrational relaxation times are given and also that of the boundary layer corrections.

5.2 Expressions for rate constants:-

In all these calculations, the expressions used for recombinational rate constant k_r and the vibrational relaxation time τ_v are those given in Ref. 13:

$$k_r = \exp(51.690911) T^{-2.12} \text{ cm}^6/\text{mole}^2 \text{ sec.} \quad (111)$$

$$p\tau_v = 20308.692 \exp(-0.6464 T^{1/3}) \text{ dynes sec/cm}^2 \quad (112)$$

Glass and Takano (Ref. 5) in their calculations of nonequilibrium flow of pure dissociated oxygen around a corner with a vibrational equilibrium model have used a constant value of $k_r = 0.67 \times 10^{15} \text{ cm}^6/\text{mole}^2 \text{ sec}$ in the temperature of range of 2500°K to 4000°K . Since in the present calculations, the temperature range was much larger, say, starting with about 5000°K in the reservoir to about 700°K at the end of the primary nozzle, it was considered necessary to use a more realistic temperature dependence of k_r so that the above expression is used. To take into account the unharmonicity for oxygen vibration, the partition function and the vibrational energy are written as sums and the vibrational energy for level j is taken to be given by

$$E_j = 1580.361 \left(j + \frac{1}{2}\right) - 12.073 \left(j + \frac{1}{2}\right)^2 + 0.0546 \left(j + \frac{1}{2}\right)^3 - 787.169 \text{ cm}^{-1} \quad (113)$$

from Ref. 22. The equilibrium constant K_c used in the rate equation (84) is given by (See Appendix B, Eq. (B85))

$$K_c = \frac{4P}{m_a} \cdot \left(\frac{T}{\theta_v}\right)^{1/2} (1 - e^{-\theta_v/T}) e^{-\theta_v/T} \quad (114)$$

which can be derived from Eqs. (60), (A34), (A31), and (A14). From the oxygen dissociation experiments of Byron (Ref. 33) , the relative efficiency

of oxygen atoms and molecules is found to be

$$\frac{k_d}{k_{dx}} = \lambda = 35 \frac{T}{\theta_p} \quad (115)$$

and this value is used in all the calculations (See also Appendix B).

5.3 Procedure for numerical calculations:-

It was already pointed out in Section 4.2.3 and 4.2.4 that the integration of the nonequilibrium equations poses three problems: (i) starting conditions, (ii) determination of nonequilibrium mass flow, and (iii) passing through the critical point $M_f = 1$ and these were considered in a general way. The specific procedure used is outlined below. As was discussed in section 4.2.4, the starting conditions were taken to be equilibrium conditions with discontinuities in derivatives.

5.3.1 Nonequilibrium mass flow

The critical mass flow m_f for fully frozen flow is greater than m_e for equilibrium flow. The evaluation of the nonequilibrium critical mass flow must be done only for nonequilibrium calculations starting upstream of the geometrical throat. For nonequilibrium calculations starting downstream of the geometrical throat, the mass flow is that of equilibrium flow since up to the starting point, the flow is considered to be in equilibrium. Thus for calculations starting upstream of the geometrical throat, initially a mass flow somewhere in between m_e and m_f is chosen and is written as

$$m_{xe1} = \text{facmne1} \times m_e$$

which defines facmne1 from the chosen m_{xe1} and known m_e , and m_f are given as lower and upper limits for m_{xe} . With this m_{xe1} , the starting or initial conditions are calculated as a solution of the algebraic equations for equilibrium flow. With these initial conditions and the mass flow m_{xe1} , the equations were integrated until either M_{f1} or $M_f = M_{f \max} < 1$ is obtained. In the former case facmne is increased such that

$$(\text{facmne})_2 = 1/2 \left((\text{facmne})_1 + \frac{m_f}{m_{xe1}} \right)$$

while in the latter case, it is reduced such that

$(\text{facmne})_2 = 1/2 \left((\text{facmne})_1 + m_f/m_{xe1} \right)$ where facmne_2 , facmne_2' are the new values of facmne .

and new upper and lower limits on m_{xe1} are given as

$$m_{xe1} < m_{xe} < m_f$$

when $M_{f \max} < 1$ and

$$m_{xe1} > m_{xe} > m_e$$

when $M_f \approx 1$. In the next step similarly a new facmne is calculated. For example, if the first two iterations give a $(\text{facmne})_1$ for which $M_f \approx 1$ and a facmne_2 for which $M_{f \max} < 1$, the new (facmne) is taken as

$$\text{facmne} = 1/2 (\text{facmne } 1 + \text{facmne } 2)$$

with the limits on facmne as

$$\text{facmne } 1 < \text{facmne} < \text{facmne } 2$$

which mean that

$$\text{facmne } 1. \quad m_e < m_{xe} < \text{facmne } 2 \quad m_e$$

This iteration process was continued until facmne 1 and facmne 2 differed in their last significant figure used in the computations (in the present work it was the eighth figure). In other words, in the final case

$$\text{facmne } 1 - \text{facmne } 2 = 1 \times 10^{-7}$$

This determines m_{xe} and the critical point.

5.3.2 Passing through the critical point $M_f = 1$

In the perfect gas case, the only equation to be integrated is

$$\frac{dT_t}{dx} = \frac{q^2 \frac{dA}{dx}}{h_T (1 - M^2)}$$

Since for expansion in the downstream part of the nozzle $M > 1$ and $\frac{dA}{dx} < 0$, one can pass through the critical point by taking $x > 0$ and a $T_t < T_t^*$ where T_t^* is the throat value which could be determined a priori. The same can be done for the equilibrium or frozen gas flows since $M=1$ is again obtained at $x = 0$ and T_t^*, α^* are known a priori. However, in the nonequilibrium case, the point where $M_f = 1$ is approached only as a limit, and also T_t^*, T_v^*, α^* are unknown. Thus one has to give a set of values $\Delta x, \Delta T_t, \Delta T_v, \Delta \alpha$ and do the calculations for

$$T_t = T_t + \Delta T_t$$

$$T_v = T_v + \Delta T_v$$

$$\alpha = \alpha' + \Delta \alpha$$

$$x = x' + \Delta x$$

where x', α', T_v', T_t' are the limiting values obtained for the lower limit on m_{xe} . This has to be repeated until the calculations proceed forward giving supersonic flow.

Another interesting situation was found with regard to the behaviour of the numerator and denominator in dT_t/dx .

Let SUM and DIFF denote

$$\text{SUM} = \frac{1}{A} \frac{dA}{dx} - \frac{1}{1+\alpha} \frac{d\alpha}{dx} + \left(\frac{1}{T(1+\alpha)} - \frac{1}{q^2} \left[\frac{3}{2} T - \epsilon_v + \theta \right] \frac{d\alpha}{dx} + (1-\alpha) \frac{d\epsilon_v}{dx} \right]$$

$$\text{DIFF} = 1 - M_f^2$$

For all M_{xe} such that $M_{f_{\max}} < 1$, SUM changes from negative to positive values smoothly as one passes through the point where $M_{f_{\max}}$ is obtained. But for all M_{xe} such that $M_f \approx 1$, SUM reached a minimum well before the point $M_f = 1$, while being negative all the while and began decreasing very rapidly as $M_f \approx 1$ is approached because of the singularity at $M_f = 1$. Thus one has to also choose the point where this jump in the variables is to be achieved. In some earlier calculations, this was prescribed at the point where M_f began oscillating around $M_f = 1$ while ignoring the fact that SUM has already passed its minimum value and thus large jumps in χ , T_t , T_v , α were required. The choice of these jumps is not straightforward as they are interdependent.

A computer programme in Fortran II language was written to integrate the differential equations using a fourth order Runge-Kutta method. Following the suggestion of Ref. 14, the programme contained a mechanism by which the integration step size was increased as the calculations proceeded downstream in the nozzle. The integration step size at the start was varied from 10^{-5} to 10^{-8} and a value of 10^{-6} was found to be quite good. The procedure for varying the nonequilibrium mass flow and the jump conditions were also incorporated in the programme through a subroutine.

The programme was run on an IBM 7090 computer at the Institute of Computer Science of the University of Toronto. Even though each iteration for nonequilibrium mass flow determination took a small time, about 5 minutes, several iterations up to 20, were required to obtain the limits such that facmne defined in Section 5.3.1 was found to sufficient accuracy. Thus only the earlier calculations for the axisymmetric hyperbolic nozzle were done starting upstream and downstream while all the later calculations were always started downstream of the nozzle throat, at $\chi = + 0.25''$.

6. DISCUSSION OF RESULTS

6.1 Axisymmetric Hyperbolic nozzle

As explained in Section 5.1.1, the aim of these calculations is: i) to study the effect of starting point for nonequilibrium flow calculations, ii) to consider the effect of the amount of energy initially in vibration, iii) to examine the importance of the parameter U. For these purposes it was enough to make the calculations for a short distance, that is 3.0cm downstream of the geometrical throat.

6.1.1. Effect of starting point for nonequilibrium calculations

To study this effect, the calculations were done only for the most complicated case, that is the coupled non-preferential dissociation model and for the reservoir conditions $T_0 = 5900^\circ\text{K}$ and $p_0 = 82 \text{ atm}$. The non-

equilibrium calculations were started at

$$x = -0.5 \text{ cm} , \quad x = -0.1 \text{ cm} , \quad x = +.2 \quad \text{or} \quad +.3 \text{ cm}$$

where $x = 0$ is the geometrical throat.

For $x = -0.5 \text{ cm}$, the flow is very near equilibrium and in 6 minutes of IBM 7090 time, the calculation could proceed only up to $x = -0.35 \text{ cm}$.

Thus the calculation was shifted to $x = -0.1 \text{ cm}$ which, when once it passed the critical point of $M_f \approx 1$, took about 5 minutes of computer time to do the calculations up to $x = +3.0 \text{ cm}$. More details about the iterative procedure used to find the nonequilibrium mass flow and passing through the critical point are given in Appendix D. For calculations starting at $x = +.2$ or $.3 \text{ cm}$, there are no problems since the mass flow in this case is simply the equilibrium mass flow.

Figs. 4a, b, c, d show the results of these calculations. The quantities

$$T_t/T_o , \quad T_v/T_o , \quad P/P_o \quad (\text{Fig. 4a}), \quad \alpha \quad (\text{Fig. 4b}), \quad \frac{dT_t}{dx}, \quad \frac{dT_v}{dx}, \quad \frac{d\alpha}{dx}$$

(Figs. 4c, 4d) are plotted for upstream and downstream starting points. It will be seen from Figs. 4a, 4b which give results for starting at $x = -0.1$ and $+0.3 \text{ cm}$ that the variables merge into each other around $x = 1.0 \text{ cm}$, especially for T_t and T_v while the effect on p cannot be seen even from the start. However, α seems to take a little more distance before it compares favourably with the upstream calculations.

In Fig. 4c, where the comparison of the derivatives $\frac{dT_t}{dx}$, $\frac{dT_v}{dx}$, $\frac{d\alpha}{dx}$ is shown for various starting points, the dashed portion between $x = -0.35 \text{ cm}$ $x = -0.1 \text{ cm}$ is an extrapolation of the curve between $x = -0.5 \text{ cm}$ to $x = -0.35 \text{ cm}$. (Thus the derivatives also merge into each other). In the critical region the derivatives behave in a singular fashion. In Fig. 4d, the comparison between the results obtained starting at $x = -0.1 \text{ cm}$ and $x = +0.3 \text{ cm}$ are shown up to $x = +3.0 \text{ cm}$. Here again, as in the case of variables themselves, they merge around $x = 1.0 \text{ cm}$.

Thus it appears from these comparisons that if one is not interested in the finer details near the throat, the nonequilibrium calculations could be started at a point downstream of the geometric throat, without incurring significant error, thus avoiding the time consuming process of finding a nonequilibrium mass flow for starting nonequilibrium calculations upstream of the nozzle throat.

6.1.2 Effect of the relative amount of energy in vibration

One is apt to think that, where there is only a small fraction of energy in vibration, the assumption of vibrational equilibrium for the calculation of the flow properties may be realistic. In Figs. 5a, 5b the flow variables along the nozzle axis are plotted for $T_o = 5900^\circ\text{K}$ and $p_o = 9.4 \text{ atm}$.

For these conditions $\alpha_o = 0.9571$ so that about 4% of the mass of oxygen

is in molecular form and the energy in vibration is only 0.3% of that in dissociation. From Fig. 5b, it will be seen that while the vibrational equilibrium model shows that α freezes at 0.83, it freezes at 0.885 and 0.915 in the coupled nonpreferential and preferential models respectively. This difference is of the order of 7 and 10% for the two coupled models and is not negligible. From Fig. 5a, there does not seem to be much effect on pressure while on the translational and vibrational temperatures, there is an appreciable difference between the results of the preferential and nonpreferential models, for example at $x = 3.0$ cm, $T_t/T_0 = 0.04$ and 0.05 respectively for the two coupled models. The vibrational equilibrium results are taken from Ref. 8 where only the variation of α is given.

Thus it would appear that even if the energy in vibration is only 0.3% of that in dissociation, the vibrational equilibrium model may not be a very realistic one for the prediction of flow properties, the effect of this being largest on the frozen atomic mass fraction.

6.1.3 Importance of the parameter U

As is pointed out in Appendix B, in the most realistic case, one has to consider U as a function of the vibrational level as well as the translational temperature. Even for a single gas, this is quite involved and if one has to deal with a mixture of different gases, U will have to be taken different for different gases, thus making the problem a very complex one. For these reasons, it would be of interest to know how useful are some simple approximations such as $U = \infty$, in which case it drops out as an additional parameter, or $U = \theta_v/n$ where n is some number such that it can be written down directly for all the gases in a mixture, instead of calculating it for each gas as a solution of Eq. (B68) for its dependence on θ_b , θ_v , T_t .

The importance of this parameter is again brought out very clearly in Figs. 4a, 4b for $T_0 = 5900^\circ\text{K}$, $p_0 = 82$ atm and Figs. 5a, 5b for $T_0 = 5900^\circ\text{K}$ and $p_0 = 9.4$ atm. Figs. 4a, 4b show that the effect of U is quite important on T_t , T_v and α while Figs. 5a, 5b show that its effect is mainly on α . The values of these at $x = +3.0$ cm for $U = \infty$ and $U = \theta_v/6$ for the uncoupled model and for vibrational equilibrium model are given in the Table below.

TABLE III

Comparison of the flow variables for different dissociation models
Axisymmetric Hyperbolic nozzle, at $x = +3.0$ cm, $A/A^* \approx 63$.

No.	$T_0(^{\circ}\text{K})$	$p_0(\text{atm})$	Model	T_t/T_0	T_v/T_0	α	α_e
1.	5900	82	Coupled				
			$U = \theta_p/6$	0.11	0.72	0.528	0.693
			$U = \infty$	0.14	0.68	0.475	
			Uncoupled	0.17	0.61	0.445	
			vib. eqm.	0.21	0.21	0.430	
2.	5900	9.4	Coupled				
			$U = \theta_p/6$	0.04	0.83	0.915	0.957
			$U = \infty$	0.05	0.88	0.885	
			Uncoupled	0.055	0.72	0.850	
			vib. eqm.	-	-	0.830	

For case 2) by comparing α with α_e and T_t with T_v near $x=0$ in Figs. 5a, 5b, it will be seen that the flow is almost frozen. This is also clearly seen by comparing the frozen and starting values of α namely, 0.915 and 0.928 respectively for the preferential dissociation model. For this case it would appear that the assumption of completely frozen flow from the reservoir is as good as the preferential model. This can be seen by noting that T_t/T_0 for the fully frozen case is 0.035, this is also shown in the figure.

For case 1), comparison of α and α_e and T_t with T_v near $x=0$ in Figs. 4a, 4b shows that the flow is slightly out of equilibrium at the nozzle throat. From these figures and the above Table, it would appear that the effect of the value of the parameter U is quite appreciable.

Thus the parameter U appears to be quite important and it would be very enlightening to use the equation (B68) for U as a function of T_t to give a clear answer to the question posed in the beginning of this section.

6.2 UTIAS 11" x 15" Hypersonic shock tunnel:-

The preliminary calculations presented in Section 6.1 having demonstrated that the calculations could be started downstream of the throat and that the coupling of vibrational and dissociational nonequilibrium is important, some further calculations were carried out for the experimental conditions, obtainable in the UTIAS shock tunnel.

For these calculations U was always taken to be equal to $\theta_D/6$ and all calculations were started at 0.25" downstream of the geometrical throat of the primary nozzle shown in Fig. 2.

The flow deflection plate was inclined at 10° to the axis of the primary nozzle. The terminal nozzle was single wedge type with an included total angle of 15° . The entrance section to this nozzle could either be 11" x 0.4" or 11" x 0.7". Calculations were done only for the 11" x 0.4" cross section.

As explained in Section 5.11, the aim of these calculations is:

- i) to consider the effect of vibrational relaxation time, τ_v
- ii) to permit evaluation of the realistic set of U , and τ_v values by comparison with experimental data to be obtained in the near future (e. g. Ref. 45),
- iii) to consider the effect of variations in reservoir conditions,
- iv) to provide theoretical estimation of flow properties in the test section.

6.2.1 Effect of vibrational relaxation time τ_v :-

As discussed in Section 3.2.3, from theoretical (Refs. 37, 38) and experimental (Ref. 23) considerations, it appears that the vibrational relaxation times in expansion flows, (where the vibrational relaxation is from an initially higher to lower excitation), could be shorter than those behind normal shocks, where the vibrational relaxation is from an initially lower to higher excitation.

To study this effect, the calculations for the UTIAS Hypersonic shock tunnel primary nozzle were done for three values of the vibrational relaxation time, namely,

$$D\tau = \frac{\tau_{v \text{ expansion}}}{\tau_{v \text{ normal shock}}} = 1.0, 0.1, 0.05 \quad (116)$$

The values 0.1 and 0.05 were chosen since the pressure measurements of Ref. 23 for vibrational relaxation of nitrogen in a nozzle without dissociation were found to lie between theoretical values obtained by using these relaxation times. It may be noted that when there is a sufficient amount of oxygen in atomic form, the atom exchange reaction (76) could be quite important in deexciting the vibrations. However, this is not considered in the present work. It is hoped that, if the cumulative effect of the atom exchange reactions and the vibrationally excited state of the gas are going to shorten the

vibrational relaxation time for expansion flows, the effect may be studied qualitatively by reducing the vibrational relaxation times determined behind normal shocks.

The results of these calculations are plotted in Figs. 6a, 6b, 6c, 7a, 7b, 7c. When the vibrational relaxation time is shortened, the vibrational state of the gas should be nearer to the translational state of the gas, i.e. $T_v \rightarrow T_t$. As more vibrational energy is available T_t will increase slightly thus decreasing relaxation times. For a Boltzmann distribution of vibrational energy distribution, this will lead to fewer number of molecules in highly excited states as the translational temperature is reduced. Because the preferential dissociation model gives a higher efficiency for dissociation from higher vibrational levels, the number of dissociations will be smaller for shorter relaxation times. Since in this model, the recombination process is essentially independent of the vibrational state of the gas, the number of recombinations will be independent of the relaxation time. Thus the net effect of shorter relaxation time on α should be to reduce it slightly because of the reduction in the number of dissociations. Fig. 6a, 7a which give T_t/T_0 , T_v/T_0 vs. χ and Figs. 6b, 7b which give α vs. χ show these trends. It is also interesting to note that for shorter τ_v the dissociation is nearer equilibrium for a longer distance as may be seen by comparing α with α_e . Reducing the relaxation times below $D\tau = 0.1$ has no observable effect on α for both cases treated here, while there is a very small effect on T_t . For both sets of initial conditions, there seems to be an effect on pressure for variation of $D\tau$ from 1.0 to 0.1 but no variation for a further change from 0.1 to 0.05. The density does not seem to be affected at all by the change in τ_v . This effect on density and pressure can be explained from the energy and continuity equations:

$$\rho g A = \text{Constant}$$

and

$$h + \frac{g^2}{2} = \frac{7+3\alpha}{2} RT_t + (1-\alpha)RE_v + R\alpha\theta_d + \frac{g^2}{2} = \text{constant}$$

as follows:-

The decrease in α and T_v in the shorter relaxation time case decreases the vibrational and dissociational energy contribution term in h , while the increase in T_t increases the translational and rotation energy contributions (i.e. $7/2 RT_t$) from the molecules. The translational energy contribution of the atom $3\alpha/2 RT_t$ remains approximately constant since α and T_t vary in opposite directions. The net effect will be to keep h approximately constant or increase it slightly and thus g either remains constant or decreases slightly which in turn keeps ρ approximately constant or increases it slightly. From the state equation $P = \rho RT_t(1+\alpha) = \rho RT_t(1-\alpha+2\alpha)$ it will be seen that p should increase slightly for shorter relaxation times. The molecular and atomic contributions are shown separately, so that it can be seen that while the atomic contribution ($2\alpha \frac{3}{2} RT_t$) remains approximately constant because α is decreasing and T_t is increasing the molecular contribution ($(1-\alpha) \frac{7}{2} RT_t$) increases since the effects of $1-\alpha$ and

T_t both contribute in the same sense. Neglecting the decrease in the vibrational contribution relative to that in dissociation and translation-rotation, one may say that q and hence β will change appreciably if the changes in α , T_t are such that

$$\frac{7}{2} R (T_t + \Delta T_t) > R (\alpha - \Delta \alpha) \theta_b$$

$$\frac{7}{2} \frac{T_t}{\theta_b} > \frac{\alpha (1 - \Delta \alpha / \alpha)}{(1 + \Delta T_t / T_t)} \approx \alpha$$

For example if $T_t / \theta_b \approx 0.02$, $\alpha < 0.07$ or for $\frac{T_t}{\theta_b} \approx 0.1$, $\alpha < 0.35$. Such situations may occur only for relaxation for very high pressures since for a given temperature, the dissociation level decreases with increase in pressure. Thus if one wishes to ascertain the effect of T_v from experiments where density variations are measured one may be able to do so by starting with initial stagnation pressures of the order of a 1000 atm. This figure is quoted since for oxygen for such pressure and temperatures of the order of 6000°K, the initial amount of dissociation in the reservoir will be relatively small and thus will be able to satisfy the above condition. However, for such pressures, the changes in pressure will also be significant, and these are easier to measure. However, direct measurement of α more readily allow estimation of T_v . Of course the ideal measurement would be to obtain the vibrational temperature T_v directly.

The velocity $q / \sqrt{RT_0}$ and the frozen Mach number M_f is plotted in Figs. 6c, 7c. Since $M_f = q / a_f$ and

$$a_f^2 = \frac{7+3\alpha}{5+\alpha} RT_t (1+\alpha) = \beta_f^2 \frac{p}{\rho} \quad (106)$$

a decrease in α will tend to decrease β_f towards the completely undissociated limit. Because the effect of decrease in T_v is to increase p and not change β , a_f may remain roughly the same or may increase for decreasing T_v . Then the frozen Mach number M_f will decrease for decreasing T_v . Figs. 6c, 7c show that there are very small changes in q while the effect on M_f is more pronounced and further the trends are as suggested above.

Another point to be noted from Figs. 6a, 6b and 7a, 7b is that while α freezes, though at different levels for the different T_v , the vibrational temperature T_v does not. This has an important bearing on the comparison with experimental results in the test section to be discussed at a later stage.

Thus, it seems that for highly dissociated gases (Fig. 6a, 6b) reduction in T_v reduces the level at which α freezes, increase T_t slightly, and brings T_v very near to T_t , T_v does not freeze and p is slightly increased, ρ , q remain constant and M_f decreases. For the case of lower α the effect on α is negligible while the effect on all other variables is the same as in the highly dissociated case, though less pronounced.

TABLE IV

Flow properties at various points in the tunnel for the experimental conditions of Table I

Reservoir conditions		End of primary nozzle				Past deflection plate		Inviscid		Test Section		with boundary layer corrections										
M _g	p ₀ (atm)/T ₀ (°K)	Dτ	T _p /T ₀	T _v /T ₀	α	ρ _p /ρ ₀	p _p /p ₀	T _{PM} /T ₀	ρ _{PM} /ρ ₀	PPM/p ₀	T ₁ /T ₀	ρ ₁ /ρ ₀	p ₁ /p ₀	M ₁	T ₁ /T ₀	ρ ₁ /ρ ₀	p ₁ /p ₀	M ₁	Σ [*] (in)	Re _r x10 ⁺⁵		
						x10 ⁻²	x10 ⁻²		x10 ⁻²	x10 ⁻³		x10 ⁻⁴	x10 ⁻⁵				x10 ⁻⁴	x10 ⁻⁵				
9.62	39.46	4630	0.341	1.0	0.290	0.649	0.165	0.447	0.113	0.190	0.175	0.289	0.036	0.445	0.140	14.33	0.041	0.577	0.204	13.49	0.77	1.44
			0.1	0.337	0.367	0.160	0.443	0.129	0.129	0.227	0.184	0.362	0.043	0.465	0.175	13.38	0.048	0.591	0.248	12.66	0.71	1.84
		0.05	0.339	0.352	0.352	0.160	0.443	0.130	0.130	0.228	0.184	0.420	0.044	0.465	0.176	13.36	0.049	0.591	0.249	12.64	0.71	1.86
11.0	22.10	4800	0.524	1.0	0.203	0.759	0.340	0.459	0.082	0.117	0.154	0.159	0.019	0.398	0.066	18.59	0.023	0.618	0.127	16.63	1.24	0.29
		0.1	0.280	0.405	0.405	0.314	0.450	0.109	0.109	0.175	0.174	0.264	0.029	0.445	0.110	15.81	0.034	0.646	0.192	14.39	1.07	0.47
		0.05	0.286	0.345	0.345	0.314	0.450	0.111	0.111	0.180	0.176	0.274	0.029	0.449	0.114	15.63	0.035	0.650	0.197	14.25	1.06	0.49
--	22.45	4600	0.418	1.0	0.219	0.752	0.254	0.454	0.088	0.133	0.158	0.186	0.023	0.407	0.083	17.03	0.028	0.597	0.146	15.53	1.10	0.44
		0.1	0.287	0.387	0.387	0.239	0.447	0.112	0.112	0.184	0.175	0.282	0.032	0.446	0.127	14.95	0.038	0.622	0.207	13.80	0.97	0.67
		0.05	0.293	0.339	0.339	0.239	0.447	0.114	0.114	0.189	0.177	0.291	0.033	0.449	0.131	14.81	0.039	0.625	0.212	13.68	0.96	0.69
9.63	14.18	4350	0.364	1.0	0.186	0.796	0.238	0.459	0.077	0.109	0.149	0.148	0.019	0.386	0.068	18.03	0.024	0.604	0.132	16.19	1.26	0.27
		0.1	0.243	0.428	0.428	0.226	0.451	0.099	0.099	0.152	0.166	0.227	0.027	0.426	0.104	15.84	0.033	0.628	0.185	14.43	1.12	0.41
		0.05	0.253	0.351	0.351	0.226	0.449	0.102	0.102	0.160	0.169	0.242	0.029	0.431	0.111	15.53	0.034	0.632	0.194	14.17	1.10	0.44
8.03	20.82	4040	0.183	1.0	0.220	0.676	0.090	0.452	0.092	0.141	0.160	0.208	0.029	0.410	0.111	15.17	0.033	0.548	0.168	14.24	0.85	1.03
		0.1	0.268	0.359	0.359	0.090	0.448	0.110	0.110	0.179	0.174	0.286	0.037	0.441	0.151	13.83	0.041	0.572	0.218	13.06	0.77	1.45
		0.05	0.274	0.316	0.316	0.090	0.446	0.112	0.112	0.183	0.175	0.295	0.038	0.444	0.155	13.68	0.042	0.574	0.224	12.93	0.76	1.50

SUBSCRIPTS: -

0 - Reservoir conditions.

1 - Test section.

 Re_r - Reference Reynolds number. p - at the end of primary nozzle. M_g - shock Mach number.

PM - past the Prandtl-Meyer fan at the leading edge of deflection plate.

 δ^* - Boundary layer displacement thickness in inches.

The results for the other experimental conditions given in Table I are presented in Figs. 8a to 8d, 9a to 9d, 10a to 10d. All of these show the same trends as discussed above. The values of T_t , T_v , p , ρ , α at the end of the primary nozzle are given in Table IV.

6.2.2 Effect of variations in reservoir conditions:-

It was pointed out in the earlier section that there are variations of pressure in the reservoir which induce variations in reservoir temperature. It was felt to be of interest to see at least qualitatively how this will affect the pressure in the test-section. For this purpose an arbitrary condition $P_o = 22.45$ atm. and $T_o = 4600^\circ\text{K}$ which is such that its temperature is near that of case 3 and its pressure is near that of case 5 given in Table I was considered. It may be seen that the relative pressure and temperature variations are exaggerated ($\frac{22.45}{22.1}$, $\frac{4600}{4800}$ or $\frac{39.46}{22.45}$, $\frac{4630}{4600}$). This has been done to enhance the effect. The test-section results for these cases are compared in Table V below:

TABLE V

Effect of variations in reservoir conditions:

No.	ΔT	P_o	T_o	α_o	α	$\alpha_o - \alpha$	T_t/T_o	P_t/P_o inviscid	M_t	P_t/P_o with B.L.
(1)	1.	39.46	4630	0.341	0.165	0.516	0.036	0.140×10^{-5}	14.33	0.204×10^{-5}
(2)		22.45	4600	0.418	0.254	0.392	0.023	0.833×10^{-6}	17.03	0.146×10^{-5}
(3)		22.10	4800	0.524	0.340	0.351	0.019	0.655×10^{-6}	18.59	0.127×10^{-5}

(1)	0.05	39.46	4630	0.341	0.160	0.531	0.044	0.176×10^{-5}	13.36	0.249×10^{-5}
(2)		22.45	4600	0.418	0.239	0.428	0.033	0.131×10^{-5}	14.81	0.212×10^{-5}
(3)		22.10	4800	0.524	0.314	0.401	0.029	0.114×10^{-5}	15.63	0.197×10^{-5}

From this Table, it may be seen that even very large variations in reservoir pressure or temperature will effect the ratio P_t/P_o the test section only by a small amount for $\Delta T = 0.05$ or 1.0. Decreasing reservoir pressure or increasing reservoir temperature seems to decrease test section static pressure ratio P_t/P_o . Since the main uncertainty in the reservoir conditions is that of temperature, which is not measured, a rough estimation of this effect may be made by taking the temperature ratios and the test-section static pressure ratios between cases (2) and (3), denoted by T_{023} , p_{t23} and the ratio p_{t23}/T_{023} denoted by TPR.

For $\Delta T = 1.0$,

$$T_{023} = \frac{(T_o)_2 = 4600}{(T_o)_3 = 4800} = 1.043$$

$$\frac{(P_t/P_o)_2}{(P_t/P_o)_3} = \frac{.833}{.655} = 1.272 \quad \text{TPR} = 1.220$$

For $D\tau = 0.05$

$$\frac{(T_0)_2}{(T_0)_3} = \frac{4800}{4600} = 1.043 \quad \frac{(P_1/P_0)_2}{(P_1/P_0)_3} = \frac{.131}{.114} = 1.149, \quad TPR = 1.102$$

with boundary layer taken into account TPR for $D\tau = 1.0$ is 1.103 and for $D\tau = 0.05$ is 1.032.

Taking T_{02} of Table I as the possible correct temperature, the change in $(P_1/P_0)_{theo}$ for changes from T_{0theo} to T_{02} are calculated below as $(P_1/P_0)_{estimated} = (P_1/P_0)_{theo} * TPR * (T_0)_{theo}/T_{02}$.

TABLE VI

Possible effect of uncertainty in reservoir temperature on test section static pressure:

No.	$D\tau$	M_s	$(T_0)_{theo}/T_{02}$	$(P_1/P_0)_{theo}$ Inviscid	$(P_1/P_0)_{estimated}$	$(P_1/P_0)_{theo}$ With B. L.	$(P_1/P_0)_{estimated}$
(1)	1.0	8.03	1.020	0.111×10^{-5}	0.125×10^{-5}	0.168×10^{-5}	0.189×10^{-5}
(2)		9.62	1.007	0.140×10^{-5}	0.172×10^{-5}	0.204×10^{-5}	0.227×10^{-5}
(3)		9.63	1.033	0.681×10^{-6}	0.858×10^{-6}	0.132×10^{-5}	0.150×10^{-5}
(4)		11.00	1.011	0.655×10^{-6}	0.808×10^{-6}	0.127×10^{-5}	0.142×10^{-5}
(1)	0.05	8.03		0.155×10^{-5}	0.174×10^{-5}	0.224×10^{-5}	0.236×10^{-5}
(2)		9.62		0.176×10^{-5}	0.195×10^{-5}	0.249×10^{-5}	0.259×10^{-5}
(3)		9.63		0.111×10^{-5}	0.126×10^{-5}	0.194×10^{-5}	0.207×10^{-5}
(4)		11.00		0.114×10^{-5}	0.127×10^{-5}	0.197×10^{-5}	0.206×10^{-5}

Table V also gives the ratios T_1/T_0 , $\frac{\alpha_0 - \alpha}{\alpha_0}$ and M_1 . From the Table it will be seen that the effect of increasing reservoir pressure or decreasing reservoir temperature is to decrease the first two ratios while it increases M_1 .

6.2.3 Realistic set of U, τ_v values:-

The effect of the parameter U in the dissociation rate expression and of τ_v the vibrational relaxation time on the flow properties in the nozzle was considered in detail in section 6.1.3 and 6.2.1 wherein it was found that both of these effect considerably T_t , T_v , α , and to a lesser extent P and M_f . By comparing the theoretically obtained results with experiment, one should be able to determine values of U and τ_v values which may be used in the rate equations.

6.3 Other Points of General Interest

6.3.1 Coupling Factor:

It was pointed out in Section 4.1.1.4 that the coupling factor V , which is the ratio of $k_{dn\ eq}$ for vibrational nonequilibrium and k_{deq} for vibrational equilibrium, would have to start with a value equal to 1 at the start of the nonequilibrium calculations and would have to increase as the flow departs from equilibrium and then should decrease and finally tend to zero as dissociation freezes out.

To demonstrate this point, the coupling factor V is plotted as a function of area ratio in Figs. 11a-d. Fig. 11a shows the effect of the parameter U in the dissociation rate constant while Figs. 11c-d show the effect of τ_v for three different cases with U fixed at $\theta_D / 6$.

From Figs. 4a, 4b, for T_t/T_0 , T_v/T_0 , α , α_e for $T_0 = 5900^\circ\text{K}$ and $p_0 = 82\text{ atm.}$, it is seen that T_v and α begin to freeze rapidly around $A/A^* \approx 5$. From Fig. 11a, which gives the coupling factor for this case, it is seen that around this area ratio V increases rapidly. V is seen to be larger for the preferential model than that for the non-preferential model because of the relative amount of nonequilibrium and different freezing values of α , T_v as seen from Figs. 4a, 4b. At an area ratio of $A/A^* \approx 63$, it was found that $V_{\text{Pref}} \approx 10^{33}$ and $V_{\text{nonpref}} \approx 10^{23}$ and they were still increasing.

From Figs. 11b to 11d, it will be seen that the effect of decreasing τ_v from its normal shock value, while keeping U constant at $\theta_D / 6$, is to slow down the increase in V up to a much larger area ratio and even shows towards the end a decreasing trend as was expected in Section 4.1.1.4. The $D\tau = 1.0$ curves in these figures correspond to the preferential case of Fig. 11a and show the same behaviour as in Fig. 11a. The decreasing trend towards the end of the primary nozzle is shown by all the three sets of reservoir conditions for $D\tau = 0.05$ while for $D\tau = 1.0$, it is shown only for $p_0 = 22.45\text{ atm.}$, $T_0 = 4630^\circ\text{K}$. V reaches much smaller values in this case compared to those of $p_0 = 22.1\text{ atm.}$, $T_0 = 4800^\circ\text{K}$ in Fig. 11d. This means that for high reservoir pressures leading to smaller initial amounts of dissociation in the reservoir, the effect of the coupling of dissociation with vibrational nonequilibrium is not as large as it is for low reservoir pressures which give higher amount of dissociation initially. This is already shown in Figs. 6b and 7b discussed in Section 6.2.1 where the effect of $D\tau$ variation on the freezing value of α is seen to be much smaller for the high pressure case of Fig. 6b than for the low pressure case of Fig. 7b.

6.3.2 Relaxation lengths:-

The quantities q/ψ and $q\tau_v$ occurring in the dissociational and vibrational rate equations

$$\frac{d\alpha}{d\tau} = \frac{\psi}{q} (VL - 1)$$

and
$$\frac{d\bar{\alpha}}{dx} = \frac{\bar{\epsilon}_\infty - \bar{\epsilon}_v}{\bar{\tau}_v} - \frac{(\bar{E} - \bar{\epsilon}_v)\psi VL}{\bar{\tau}(1-\alpha)} + \frac{(\bar{G} - \bar{\epsilon}_v)\psi}{\bar{\tau}(1-\alpha)}$$

have the dimensions of length and are defined as characteristic relaxation lengths for dissociation and vibration. Rewrite these rate equations as follows:

$$\frac{d\alpha}{dx} = \frac{\alpha - \alpha_{el}}{\tau_d} \quad (117)$$

and
$$\frac{d\epsilon_v}{dx} = \frac{\epsilon_\infty - \epsilon_v}{\tau_v} \quad (118)$$

where
$$\tau_d = \frac{q}{\psi} (\alpha - \alpha_{el}) / (VL-1) \quad (119)$$

$$\tau_v = \left[\frac{1}{\bar{\tau}_v} - \frac{\psi VL(\bar{E} - \bar{\epsilon}_v)/(\epsilon_\infty - \epsilon_v)}{\bar{\tau}(1-\alpha)} + \frac{\psi(\bar{G} - \bar{\epsilon}_v)/(\epsilon_\infty - \epsilon_v)}{\bar{\tau}(1-\alpha)} \right]^{-1} \quad (120)$$

and α_{el} is the local equilibrium value of α . When vibration and dissociation are very near equilibrium, then $\alpha \approx \alpha_{el}$ and $\epsilon_\infty \approx \epsilon_v$.

Thus
$$\left| \frac{d\alpha}{dx} \right| = \left| \frac{\alpha - \alpha_{el}}{\tau_d} \right| \ll \frac{\alpha_{el}}{\tau_d} \quad \text{Since } |\alpha - \alpha_{el}| \ll \alpha_{el} \quad (121)$$

and
$$\left| \frac{d\epsilon_v}{dx} \right| = \left| \frac{\epsilon_\infty - \epsilon_v}{\tau_v} \right| \ll \frac{\epsilon_\infty}{\tau_v} \quad \text{Since } |\epsilon_\infty - \epsilon_v| \ll \epsilon_\infty \quad (122)$$

When vibration and dissociation are very nearly frozen $\alpha_{el} \ll \alpha$ and

$$\epsilon_\infty \ll \epsilon_v \quad \text{or } |\alpha - \alpha_{el}| \gg \alpha_{el} \quad \text{and } |\epsilon_\infty - \epsilon_v| \gg \epsilon_\infty$$

Thus
$$\left| \frac{d\alpha}{dx} \right| = \left| \frac{\alpha - \alpha_{el}}{\tau_d} \right| \gg \frac{\alpha_{el}}{\tau_d} \quad (123)$$

$$\left| \frac{d\epsilon_v}{dx} \right| = \left| \frac{\epsilon_\infty - \epsilon_v}{\tau_v} \right| \gg \frac{\epsilon_\infty}{\tau_v} \quad (124)$$

Hence the transition from equilibrium to frozen conditions means that the quantities $\frac{\tau_d}{\alpha_{el}} \left| \frac{d\alpha}{dx} \right|$ and $\frac{\tau_v}{\epsilon_\infty} \left| \frac{d\epsilon_v}{dx} \right|$ change from a value very much less than unity to a value very much greater than unity. One therefore may be able under these circumstances to predict approximately the frozen values of α and T_v by assuming that this occurs when

$$\frac{\tau_d}{\alpha_{el}} \left| \frac{d\alpha}{dx} \right| \quad \text{and} \quad \frac{\tau_v}{\epsilon_\infty} \left| \frac{d\epsilon_v}{dx} \right| \quad \text{become equal to unity.}$$

This will not help very much since this still requires the knowledge of these quantities in nonequilibrium flow. Hall and Russo (Ref. 8) in their calculations for dissociational nonequilibrium only evaluated the quantity

$\frac{r_d}{\alpha_{ee}} \left| \frac{d\alpha}{dx} \right|$ for equilibrium flow that is for infinite rates. By replacing $\left| \frac{d\alpha}{dx} \right|$ by $\frac{1}{2} \left| \frac{d\alpha_{ee}}{dx} \right|$ and α_{ee} by $1/2 \alpha_{ee}$ where α_{ee} is the infinite rate flow or complete equilibrium flow result the quantity r_d was also evaluated at the infinite rate flow values and they found that this predicts the final freezing value of α with reasonable accuracy.

If it is assumed that this may still be valid for coupled vibrational and dissociational nonequilibrium, then one may say that the frozen values and their location are obtained when

$$\left| \frac{d\alpha_{ee}}{dx} \right| = \frac{\alpha_{ee}}{r_{d\infty}} \quad (125)$$

and

$$\left| \frac{d\epsilon_{\infty}}{dx} \right| = \frac{\epsilon_{\infty}}{r_{v\infty}} \quad (126)$$

where ϵ_{∞} corresponds to the vibrational energy in complete equilibrium flow. The derivation of Eqs. (125) and (126) implicitly assumes that vibrational and dissociational nonequilibrium are uncoupled, so that Eqs. (119) and (120) for r_d and r_v are to be rewritten as

$$r'_d = \frac{g}{\psi} (\alpha - \alpha_{ee}) / (L - 1) \quad (127)$$

and

$$r'_v = g \tau_v \quad (128)$$

where primes denote the relaxation lengths for the uncoupled model. Eq. (127) may be further simplified by rewriting L in terms of α , α_{ee} as follows:

$$L = \frac{K_c m_a}{2P} \frac{(1-\alpha)}{\alpha^2} = \frac{\alpha_{ee}^2}{1-\alpha_{ee}} \frac{(1-\alpha)}{\alpha^2} \quad (129)$$

since the local equilibrium constant K_c and the local equilibrium α_{ee} are related through Eq. (60). Hence

$$\begin{aligned} L - 1 &= \frac{\alpha_{ee}^2 (1-\alpha) - \alpha^2 (1-\alpha_{ee})}{\alpha^2 (1-\alpha_{ee})} \\ &= (\alpha_{ee} - \alpha) \left[\frac{\alpha_{ee}}{\alpha^2 (1-\alpha_{ee})} + \frac{1}{\alpha} \right] \end{aligned} \quad (130)$$

and

$$|r'_d| = \frac{g}{\psi} \frac{\alpha_{ee} - \alpha}{\alpha_{ee} - \alpha} \left[\frac{\alpha_{ee}}{\alpha^2 (1-\alpha_{ee})} + \frac{1}{\alpha} \right] = \frac{g}{\psi} \left[\frac{\alpha_{ee}}{\alpha^2 (1-\alpha_{ee})} + \frac{1}{\alpha} \right] \quad (131)$$

By evaluating this at equilibrium conditions, one has

$$r_{d\infty} = \frac{g_e}{\psi_e} \frac{2 - \alpha_e}{\alpha_e (1 - \alpha_e)} \quad (132)$$

and

$$r_{v00} = g_e \tau_{ve} \quad (133)$$

where the subscript e denotes complete equilibrium flow values. For the coupled model r_d cannot be simplified to the form (131) because the factor V rapidly becomes larger than unity. To see how much r_d differs from q/ψ because of the factor $(VL-1)/(\alpha - \alpha_{el})$ and also how much r_v differs from $g\tau_v$ and how much these differ from g_e/τ_e and $g_e\tau_{ve}$ and the effect of the parameters U , DT on g/ψ and g/τ_v ; the following quantities have been computed, namely,

$$DRL = r_{de} = |\alpha_{el} - \alpha| / \frac{d\alpha}{dx} \quad (D87)$$

$$DRLI = g/\psi = r_{deI} \quad (D88)$$

$$VERL = r_{ve} = (\epsilon_{\infty} - \epsilon_v) / \frac{d\epsilon_v}{dx} \quad (D85)$$

$$VERLI = g\tau_v = r_{veI} \quad (D86)$$

where the quantities on the left hand side are Fortran names and ζ is a non-dimensionalisation constant defined in Appendix D. These are plotted in Figs. 12a-12h. The way in which the quantities rd_1 , rv_1 , rv_1 differ from each other as the degree of nonequilibrium increases can be seen as follows. At the beginning when everything is near equilibrium, $\alpha \approx \alpha_{el}$, $T_v \approx T_e$, $V \approx 1$ and thus using Eq. (130) and replacing α_{el} by α

$$\begin{aligned} rd_e &= \frac{g}{\psi} (\alpha - \alpha_{el}) / (VL - 1) \\ &\approx \frac{g}{\psi} (\alpha - \alpha_{el}) / (L - 1) \\ &\approx \frac{g}{\psi} / \left[\frac{\alpha_{el}}{\alpha^2(1 - \alpha_{el})} + \frac{1}{\alpha} \right] \approx \frac{g}{\psi} \frac{\alpha(1 - \alpha)}{(2 - \alpha)} \approx \frac{\alpha(1 - \alpha)}{(2 - \alpha)} r_{deI} \end{aligned} \quad (134)$$

or

$$r_{de} < r_{deI} \quad (135)$$

and also $\bar{G} \approx \bar{E}$ thus from Eq. (120)

$$\begin{aligned} rv_1 &= \left[\frac{1}{g\tau_v} - \frac{\psi VL (\bar{E} - \epsilon_v) / (\epsilon_{\infty} - \epsilon_v)}{g(1 - \alpha)} + \frac{\psi (\bar{G} - \epsilon_v) / (\epsilon_{\infty} - \epsilon_v)}{g(1 - \alpha)} \right]^{-1} \\ &\approx \left[\frac{1}{g\tau_v} - \frac{\psi}{g} \frac{(VL - 1)}{1 - \alpha} \frac{(\bar{G} - \epsilon_v)}{(\epsilon_{\infty} - \epsilon_v)} \right]^{-1} \\ &\approx \left[\frac{1}{g\tau_v} - \frac{1}{r_{de}} \frac{\alpha - \alpha_{el}}{1 - \alpha} \frac{(\bar{G} - \epsilon_v)}{(\epsilon_{\infty} - \epsilon_v)} \right]^{-1} \\ &\approx \left[\frac{1}{g\tau_v} - \frac{1}{r_{deI}} \frac{\alpha(\alpha - \alpha_{el})}{(2 - \alpha)} \frac{\bar{G} - \epsilon_v}{\epsilon_{\infty} - \epsilon_v} \right]^{-1} \end{aligned} \quad (136)$$

$$\approx \left[\tau_v \left[1 - \frac{\bar{n}_{ve,1}}{\bar{n}_{de,1}} \frac{\alpha(\alpha - \alpha_{el})}{(2-\alpha)} \frac{\bar{G} - \bar{E}_v}{\bar{E}_a - \bar{E}_v} \right]^{-1} \approx \bar{n}_{ve,1} \left[1 - \frac{\bar{n}_{ve,1}}{\bar{n}_{de,1}} \frac{\alpha(\alpha - \alpha_{el})}{(2-\alpha)} \frac{\bar{G} - \bar{E}_v}{\bar{E}_a - \bar{E}_v} \right]^{-1}$$

or $r_{v1} > r_{v11}$ (137)

As frozen values of T_v and α are approached, $\alpha_{el} \rightarrow 0$ and

$$\begin{aligned} \bar{n}_{de} &= \frac{\bar{g}}{\bar{\psi}} \frac{\alpha - \alpha_{el}}{VL - 1} \\ &= \frac{\bar{g}}{\bar{\psi}} \frac{\alpha - \alpha_{el}}{\left[V \frac{\alpha_{el}^2 (1-\alpha)}{(1-\alpha_{el}) \alpha^2} - 1 \right]} \\ &\approx \alpha \cdot \frac{\bar{g}}{\bar{\psi}} \approx \alpha \cdot \bar{n}_{de,1} \\ r_{v1} &= \left[\frac{1}{\bar{g} \tau_v} + \frac{\bar{\psi}}{\bar{g}} \frac{(\bar{G} - \bar{E}_v)}{\bar{E}_a - \bar{E}_v} \frac{1}{1-\alpha} - \frac{\bar{\psi} VL}{\bar{g}(1-\alpha)} \frac{\bar{E} - \bar{E}_v}{\bar{E}_a - \bar{E}_v} \right]^{-1} \\ &\approx \left[\frac{1}{\bar{g} \tau} + \frac{\bar{\psi}}{\bar{g}} \frac{\bar{G} - \bar{E}_v}{\bar{E}_a - \bar{E}_v} \frac{1}{1-\alpha} \right]^{-1} \\ &\approx \bar{n}_{ve,1} \left[1 + \frac{\bar{n}_{ve,1}}{\bar{n}_{de,1}} \frac{1}{1-\alpha} \frac{\bar{G} - \bar{E}_v}{\bar{E}_a - \bar{E}_v} \right]^{-1} \end{aligned} \quad (138)$$

Also $r_{de} < r_{d11}$ and $r_{v1} > r_{v11}$ for the same reasons given below Eq. (137). Figs. 12a to 12h show these trends, that is, we always have $r_{d1} < r_{d11}$ and $r_{v1} > r_{v11}$.

The value of r_{d11} for full equilibrium flow should be greater than r_{d11} for nonequilibrium flow since $T_{t \text{ neq}} < T_{t \text{ eq}}$ and $q_{eq} > q_{neq}$ so

$$\begin{aligned} \gamma_{neq} \propto k_h \propto T_{t \text{ neq}}^{-n} &> T_{t \text{ eq}}^{-n} \propto \gamma_{eq} \\ \bar{\tau}_{neq} \propto \frac{e^{-(T_{t \text{ neq}})}}{T_{t \text{ neq}}} &> \frac{e^{-(T_{t \text{ eq}})}}{T_{t \text{ eq}}} \propto \bar{\tau}_{eq} \end{aligned}$$

from Eqs. (86), (111), (112). Thus

$$(\bar{n}_{de,1})_{eq} = \frac{\bar{g}_{eq}}{\gamma_{eq}} > \frac{\bar{g}_{neq}}{\gamma_{neq}} = (\bar{n}_{de,1})_{neq} \quad (139)$$

and

$$(\bar{n}_{ve,1})_{eq} = \bar{g}_{eq} \bar{\tau}_{eq} < \bar{g}_{neq} \bar{\tau}_{neq} = (\bar{n}_{ve,1})_{neq} \quad (140)$$

This comparison with equilibrium values is shown in Figs. 12c and 12d where it will be seen that near the throat, when the flow is very near equilibrium $(r_{d11})_{eq} \approx (r_{d11})_{neq}$ and $(r_{v11})_{eq} \approx (r_{v11})_{neq}$ and as the nonequilibrium increases $(r_{d11})_{neq}$ and $(r_{v11})_{neq}$ curves depart from their equilibrium counterparts showing that $(r_{d11})_{eq} > (r_{d11})_{neq}$ and $(r_{v11})_{eq} < (r_{v11})_{neq}$.

The effect of the parameter U on r_{d11} and r_{v11} is similar to that of the equilibrium case, namely,

$$(\bar{n}_{de,1})_{np} > (\bar{n}_{de,1})_{pref} \quad (141)$$

$$(\bar{n}_{ve,1})_{np} < (\bar{n}_{ve,1})_{pref} \quad (142)$$

since $T_{t np} > T_{t pref}$ where the nonpreferential and preferential cases are distinguished by the subscripts np and pref respectively. These trends are shown in Figs. 12a and 12b. The differences in α_{pref} and α_{np} appear to be sufficiently large to reverse the above trends on rd_{11} , i. e. from Eq. (138),

$$(rd_{11} pref) \approx \alpha_{pref} \cdot (rd_{11} pref) > \alpha_{np} \cdot (rd_{11} np) \approx (rd_{11})_{np} \quad (143)$$

where $\alpha_{pref} > \alpha_{np}$ from Fig. 4b whereas this reversal in trend on rv_1 appears to occur only when the amount of nonequilibrium is relatively large.

From Figs. 12c to 12h, it appears that the effect of variations in vibrational relaxation time τ_v is significant only on rv_1 , rv_{11} and seems to make only slight differences on rd_1 , rd_{11} ; namely, the reduction in vibrational relaxation times reduces the vibrational relaxation lengths as is to be expected.

The question as to how good is the frozen value of α predicted on the basis of equilibrium flow results may now be answered. It is stated above that the frozen value of α may be considered as that obtained when

$$\frac{r_d}{\alpha_{el}} \left| \frac{d\alpha}{dx} \right| = 1 \quad (144)$$

or using average equilibrium flow values, from Eq. (125)

$$\frac{d\alpha_{eq}}{dx} = \frac{\alpha_{eq}}{r_{d0}} = \frac{\gamma_e}{g_e} \frac{2 - \alpha_{eq}}{1 - \alpha_{eq}} \approx \frac{\gamma_e}{g_e} = \left(\frac{1}{r_{d1}} \right)_{eq} < \left(\frac{1}{r_{d1}} \right)_{neq} \quad (145)$$

from Eqs. (125), (132) and (139). From Figs. 6b and 12c, it will be seen that $(rd_{11})_{eq}$ begins to depart from $(rd_{11})_{neq}$ when significant freezing in α begins namely $A/A^* \approx 4$. Also from Fig. 6b, it will be seen that $\frac{d\alpha_{eq}}{dx}$ is approximately equal to $\left(\frac{d\alpha}{dx} \right)_{neq}$. Thus it appears that for an

engineering approximation, the frozen value of α may be predicted reasonably well on the basis of Eq. (125) evaluated at equilibrium conditions.

Similarly the frozen value of the vibrational temperature T_v is given by the condition

$$\frac{r_v}{\epsilon_{\infty}} \cdot \left| \frac{d\epsilon_v}{dx} \right| = 1 \quad (146)$$

or evaluating at equilibrium flow values, from Eqs. (126), (133)

$$\left| \frac{d\epsilon_{eq}}{dx} \right| = \frac{\epsilon_{\infty}}{r_{v0}} = \frac{\epsilon_{\infty}}{g_e \tau_{ve}} = \frac{\epsilon_{\infty}}{(r_{ve1})_{eq}} \quad (147)$$

From Fig. 6a, it will be seen that for $D\tau = 1$, $\left(\frac{dT_t}{dx} \right)_{eq} \approx \left(\frac{dT_v}{dx} \right)_{neq}$ at the point

where T_v begins to freeze rapidly, i. e. for $\frac{A}{A^*} \approx 10$ whereas from Fig. 12d,

it will be seen that $(rvl)_{eq}$ has already deviated considerably from $(rvl)_{neq}$ for $A/A^* \approx 10$. For $D\tau = 0.05$ and 0.1 , Fig. 6a shows that T_v is freezing only slowly. However, $(rvl)_{eq}$ departs from $(rvl)_{neq}$ for $D\tau = 0.05$ around $A/A^* \approx 4.0$, and for $D\tau = 0.1$ as early as $A/A^* \approx 1.1$. Thus for $D\tau = 0.1$ and 0.05 , the criterion of Eq. (147) for freezing value of T_v does not seem to be useful, while it may be useful for $D\tau = 1.0$.

In Table VII below, the freezing criterion for α , is applied to all the cases of Table I. The values of r_{dl} , $\frac{d\alpha}{d\tau}$ and their products when this criterion

is approximately satisfied and α_f the corresponding value of α and A/A^* the corresponding area ratio, and α_f the finally frozen value of α obtained by full nonequilibrium calculations and the reservoir conditions p_0 , T_0 , α_0 are given in the Table for $D\tau = 1.0$.

TABLE VII

Comparison of α_f found by freezing criterion (144) with finally frozen α_f

= 1.0

No.	M_s	p_0 (atm)	T_0	α	A/A^*	$(r_{dl})_{neq}$	$\frac{d\alpha}{d\tau}_{neq}$	$(r_{dl} \frac{d\alpha}{d\tau})_{neq}$	α_f	α_f
1.	8.03	20.82	4040	0.183	9.99	0.970×10^{-3}	0.100×10^{-2}	0.97	0.096	0.090
2.	9.62	39.46	4630	0.341	10.34	0.256×10^{-3}	0.338×10^{-2}	0.87	0.181	0.165
3.	9.63	14.18	4350	0.364	5.12	0.152×10^{-3}	0.475×10^{-2}	0.72	0.249	0.238
4.	11.00	22.1	4800	0.524	6.27	0.843×10^{-2}	0.645×10^{-2}	0.54	0.356	0.340
5.	-	22.45	4600	0.417	9.99	0.270×10^{-3}	0.258×10^{-2}	0.70	0.264	0.254

7. CONCLUSIONS

A theoretical study has been made for quasi-one dimensional nozzle flows of pure dissociated oxygen for coupled vibrational and dissociational nonequilibrium. It is assumed that the probability for dissociation from various vibrational energy levels may be represented by an exponential function containing an adjustable parameter U . This takes into account the effect of vibrational nonequilibrium on dissociational rate. It is assumed that the vibrational nonequilibrium may be represented by a vibrational temperature which is different from the translational temperature. The effect of dissociational nonequilibrium is taken into account by modifying the classical Landau-Teller equation for vibrational relaxation through addition of two terms for the average energy lost due to dissociation and that gained due to recombination. Two values of U have been used in these calculations: 1) $U = \infty$ giving equal probability; and 2) $U = \theta_D/6$ giving higher probability for dissociation from higher levels. These two models

are called non-preferential and preferential respectively.

The effects of exchange reaction between atoms and molecules, and relaxation from higher to lower vibrational excitational state on vibrational relaxation has been studied qualitatively by shortening the vibrational relaxation times observed for flows behind normal shocks. This has been done for the preferential dissociation model only that is with $U = \theta_D/6$.

The values of the flow variables in the test-section of the UTIAS 11" x 15" Hypersonic shock tunnel were calculated by assuming the vibration and dissociation to be frozen at the end of the primary nozzle. Boundary layer corrections were applied to these inviscid conditions in the primary nozzle using an empirical formula for the evaluation of boundary layer displacement thickness for turbulent flow under the assumption of frozen boundary layer.

The results show that:

- 1) The nonequilibrium calculations may be started downstream of the geometrical throat at a point where the frozen Mach number is greater than unity, thus reducing the computer time.
- 2) Even if the amount of vibrational energy is initially small compared to that in dissociation (due to a very high degree of dissociation), one has to consider vibrational nonequilibrium and also the effect of coupling to predict a correct finally frozen value of α .
- 3) The finally frozen values of α and T_v for the preferential dissociation model are higher than the nonpreferential values. Both of these are found to be higher than those calculated for the uncoupled or vibrational equilibrium models. The translational temperature T_t for the preferential model is found to be lower than that for nonpreferential model.
- 4) Shortening of vibrational relaxation times below the normal shock values reduces the level at which the atomic mass fraction freezes finally. This reduction is more significant for nozzle expansions with a higher initial degree of dissociation. It also brings T_v nearer to T_t as is to be expected and does not show T_v to freeze even up to an area ratio of about 50. It also slightly increases the pressure while there is little effect on density.
- 5) The coupling factor, or the ratio of the dissociational rate constant for vibrational nonequilibrium and equilibrium increases rapidly as α begins to freeze rapidly. It continues to increase even up to an area ratio of $A/A^* \approx 50$ for $U = \theta_D/6$ and normal shock vibrational relaxation times. For $U = \theta_D/6$ and vibrational relaxation times shorter than those behind normal shock, it begins to drop rapidly around $A/A^* \approx 50$ after reaching a maximum. It is felt that if U is taken as a function of T_t ,

even for $\tau_v = \tau_v$ normal shock, the decreasing trend may be obtained. This U, T_t relation as derived in Appendix B is

$$\frac{e^{a/U}}{Q(-U)} = \frac{Z_0}{a T_t^n Q(T_t)}$$

where a is known constant, Z_0 is the collision number, θ_D is characteristic temperature for dissociation and $Q(T_t)$, $Q(-U)$ are given by

$$\begin{aligned} Q(T_t) &= \sum e^{-E_j/kT_t} \\ Q(-U) &= \sum e^{E_j/kU} \end{aligned}$$

6) For a fast and approximate evaluation of the finally frozen value of α , the criterion that the product of the dissociational relaxation length r_{dl} and the $\frac{d\alpha}{dx}$, evaluated from equilibrium results be of order unity, seems to be good.

7) It is anticipated that comparison of the theoretical computations given here with experimental measurements of α taken in the UTIAS 11" x 15" Shock Tunnel (Ref. 45) will enable realistic values of τ_v and U to be determined.

8. SUGGESTIONS FOR FURTHER WORK

Two important modifications can be carried out immediately:-

- 1) Use of a proper U, T_t relation given above instead of taking U constant and independent of T_t .
- 2) Taking account of the atom-molecule exchange reaction in the vibrational relaxation equation by means of the rate constants given in Eq. (87).
- 3) Modifying the fractional number of collisions $M(D-E_j)$ with relative energy greater $D-E_j$ to take into account the internal energies of the particles entering into collision, i. e. writing

$$M(D-E_j) = (D-E_j/kT_t)^{\mathcal{L}} / \mathcal{L}! e^{-(D-E_j)/kT_t}$$

instead of the exponential factor alone, where $\mathcal{L} = 1, 2$ for atom-molecule and molecule-molecule collisions respectively.

- 4) Application of this model to the flow around a corner to see if a de-excitation shock occurs behind the tail of the expansion fan as found by Glass and Takano (Ref. 5) with vibrational equilibrium model. (This work is already in progress - July, 1966).

REFERENCES

1. Cleaver, J. W. The Two-Dimensional Flow of an Ideal Dissociating Gas, Report No. 123, College of Aeronautics, Cranfield, Dec. 1959.
2. Appleton, J. P. The Structure of a Centered Rarefaction Wave in an Ideal Dissociating Gas, U. S. A. A. Report No. 136, Department of Aeronautics and Astronautics, University of Southampton, April, 1960.
3. Appleton, J. P. The Structure of a Prandtl-Meyer Expansion fan in an Ideal Dissociating Gas, U. S. A. A. Report No. 146, Department of Aeronautics and Astronautics, University of Southampton, August, 1960.
4. Freeman, N. C. The Dynamics of a Dissociating Gas, Part II, Non-Equilibrium Theory, J. F. M. Vol. 4, Part 4, 1958.
5. Glass, I. I. and Takano, A. Non-Equilibrium Expansion Flow of Dissociated Oxygen Around a Corner, UTIA Report No. 91, June, 1963.
6. Der, J. J. Theoretical Studies of Supersonic Two-Dimensional and Axi-Symmetric Non-Equilibrium Flow, NASA TRR-164, 1963.
7. Arave, R. J. Centered Rarefaction Wave in a Chemically Reacting Gas, Report No. D2-22534, Boeing Co., 1963.
8. Hall, J. G. and Russo, A. L. Studies of Chemical Non-Equilibrium in Hypersonic Nozzle Flows, Report No. AD-1118-A-6, Cornell Aeronautical Laboratory, November, 1959.
9. Clarke, J. F. The Linearised Flow of a Dissociating Gas, J. F. M., Vol. 7, Part 4, 1960.
10. Eschenroeder, A. Q., Boyer, D. W. and Hall, J. G. Exact Solutions for Non-Equilibrium Expansions of Air with Coupled Chemical Reactions, Report No. AF-1413-A-1, Cornell Aeronautical Laboratory, May, 1961.

11. Lordi, J. A. and Mates, R. E. Non-Equilibrium Expansions of High Enthalpy Air Flows, Report No. ARL 64-206, November, 1964.
12. Blythe, P. A. Asymptotic Solutions in Non-Equilibrium Nozzle Flow, NPLAERO. Report 1071, September, 1963.
13. Vincenti, W. G. Calculations of the One-Dimensional Non-Equilibrium Flow of Air Through a Hypersonic Nozzle, AEDC-TN-61-65, May, 1961.
14. Emanuel, G. and Vincenti, W. G. Method for Calculation of the One-Dimensional Non-Equilibrium of a General Gas Mixture Through a Hypersonic Nozzle, AEDC-TDR-62-131, June, 1962.
15. Nagamatsu, H. T. and Sheer, R. E., Jr. Vibrational Relaxation and Recombination of Nitrogen and Air in Hypersonic Nozzle Flows, Report No. 63-RL-(3429C), General Electric Research Laboratory, September, 1963.
16. Heims, S. P. Effects of Chemical Dissociation and Molecular Vibrations on Steady One-Dimensional Flow, NASA TN-D-87, August, 1959.
17. Clarke, J. F. Relaxation Effects on the Flow Over Slender Bodies, J. F. M., Volume II, Part 4, 1961.
18. Wood, A. D., Springfield, J. F. and Pallone, A. J. Determination of the Effects of Chemical and Vibrational Relaxation on an Inviscid Hypersonic Flow Field, AIAA preprint No. 63-441, AIAA Conference on Physics of Entry into Planetary Atmospheres.
19. Hammerling, P., Teare, J. D. and Kivel, B. Theory of Radiation from Luminous Shock Waves in Nitrogen, Research Report 49, AVCO Everett Research Laboratory, June, 1959.
20. Treanor, C. E. and Marrone, P. V. Effect of Dissociation on the Rate of Vibrational Relaxation, Physics of Fluids, Vol. 5, No. 9, September, 1962.
21. Treanor, C. E. and Marrone, P. V. Vibration and Dissociation Coupling Behind Strong Shock Waves, Paper presented at Symposium on Dynamics of Manned Lifting Planetary Reentry, October, 1962.

22. Marrone, P. V. Inviscid Non-Equilibrium Flow Behind Bow and Normal Shock Waves, Report No. QM-1626-A-12(I), Cornell Aeronautical Laboratory, May, 1963.
23. Hurle, I. R., Russo, A. L. and J. G. Hall. Experimental Studies of Vibrational and Dissociative Non-Equilibrium in Expanded Gas Flows, Paper presented at AIAA Conference on Physics of Entry into Planetary Atmospheres, held at Boston, August, 1963.
24. Fitts, D. D. Non-Equilibrium Thermodynamics, McGraw Hill Book Co. Inc., 1962.
25. Wood, W. W. and Kirkwood, J. G. Hydrodynamics of a Reacting and Relaxing Fluid, J. of App. Phy., Vol. 28, No. 4, April, 1957.
26. Eschenroeder, A. R. Entropy Changes in Non-Equilibrium Flows, Physics of Fluids, Vol. 6, No. 10, October, 1963.
27. Mates, R. E. and Weatherston, R. C. Definition of Temperature in Non-Equilibrium Processes, Physics of Fluids, Vol. 8, No. 4, April, 1965.
28. Treanor, C. E. Coupling of Vibration and Dissociation in Gasdynamic Flows, AIAA paper No. 65-29, presented at AIAA 2nd Aerospace Sciences Meeting, January, 1965.
29. Hutchinson, E. Physical Chemistry, W. B. Saunders Co., 1962.
30. Laidler, K. J. Reaction Kinetics, Vol. I, Homogeneous Gas Reactions, Pergamon Press, 1963.
31. Fowler, R. H. and Guggenheim, E. A. Statistical Thermodynamics, Cambridge University Press, 1952, Chap. XII.
32. Matthews, D. L. Interferometric Measurement in the Shock Tube of the Dissociating Rate of Oxygen, Physics of Fluids, Vol. 2, No. 2, 1959.
33. Byron, S. R. Measurement of the Rate of Dissociation of Oxygen, J. Chem. Phy., Vol. 30, No. 6, 1959.

34. Wray, K. L. Kinetics of O_2 Dissociation and Recombination, Preprint for Tenth Symposium (International) On Combustion, 1964.
35. Hertzfeld, K. F. Theories of Relaxation Times, Proceedings of Italian Physical Society on Dispersion and Absorption of Sound by Molecular Processes, Academic Press Inc., N. Y. 1963.
36. Widom, B. Inelastic Molecular Collisions with a Maxwellian Interaction Energy, J. Chem. Phy. Vol. 27, 1957.
37. Alterman, E. B. and Wilson, D. J. Vibrational Energy Transfer in Gases; Atom-Diatomic Molecule Collisions, J. Chem. Phy., Vol. 42, No. 6, March, 1965.
38. Wild, E. On the Theory of Vibrational Relaxation in Gases, Report. No. ARC 24617, Aeronautical Research Council, England, March, 1963.
39. Burke, A. F. and Bird, K. D. The Use of Conical and Contoured Expansion Nozzles in Hypervelocity Facilities Advances, in Hypervelocity Techniques, Plenum Press, N. Y., 1962.
40. Hartunian, R. A. and Marrone, P. V. Heat Transfer from Dissociated Gases in a Shock Tube, Rept. No. AD-1118-A17, Cornell Aeronautical Laboratory, November, 1959.
41. Clarke, J. F. The Flow of Chemically Reacting Gas Mixtures, CoA Report No. 117, The College of Aeronautics, Cranfield, November, 1958.
42. Burke, A. F. Turbulent Boundary Layers on Highly Cooled Surfaces at High Mach Numbers, Rept. No. 118, Cornell Aeronautical Lab., November, 1961.
43. Clarke, J. F. and McChesney, M. The Dynamics of Real Gases, Butterworths and Co. Ltd., London, 1964.
44. Herzberg, G. Spectra of Diatomic Molecules, 2nd Edition, Van Nostrand, 1950.
45. Reddy, N. M. Measurements of Hypersonic Free Stream Oxygen Atom Concentration Using a Self Calibrating Catalytic Probe, UTIAS Report to be published.

NUMERICAL CONSTANTS

Universal Constants:-

Boltzmann constant	$k = 1.380 \times 10^{-16} \text{ erg/}^{\circ}\text{K}$
Planck constant	$h = 6.620 \times 10^{-27} \text{ erg. sec.}$
Avogadro number	$N_A = 6.027 \times 10^{23} \text{ per mole.}$

Constants for Oxygen:-

m_a	=	16 gm/mole	
g_{01}	=	9)
g_{02}	=	3)
θ_r	=	2.08 $^{\circ}$ K)
θ_d	=	59390 $^{\circ}$ K)

Eq. (A. 16)

APPENDIX A

Thermodynamic Equations

With the assumptions I) to V) of Section 2, the thermodynamic properties of a pure dissociating diatomic gas in vibrational and chemical nonequilibrium can be derived. The gas mixture is composed of atoms and molecules and divided into two subsystems, I) consisting of the translation and rotational degrees of freedom of the atoms and molecules at temperature T_t , and II) the vibrational degrees of freedom at temperature T_v .

Let N_j be the number of j particles in the volume V and $f_j^{(t)}$, $f_j^{(r)}$, $f_j^{(v)}$ be the partition functions associated with the translational, rotational and vibrational degrees of freedom ($j=1$ and 2 for atoms and molecules respectively). Then the Helmholtz free energy A of the mixture for the total number of particles $N = \sum N_j$ in the volume V is (Ref. 29)

$$A = A_t + A_r + A_v \quad (A1)$$

where

$$A_t + A_r = -kT_t \sum_j N_j \left[\log f_j^{(t)} - \log N_j + 1 + \log f_j^{(r)} \right] \quad (A2)$$

$$A_v = -kT_v \sum_j N_j \log f_j^{(v)} \quad (A3)$$

A_t , A_r , A_v being the Helmholtz free energy for the subsystems consisting of the translational, rotational and vibrational degrees of freedom respectively. The partition function is

$$f_j^{(t)} = \frac{(2\pi m_j k T_t)^{3/2}}{h^3} V \cdot g_{oj} e^{-\epsilon_{oj}/kT_t} \quad (A4)$$

where

ϵ_{oj} = excess energy of the ground states of the j particles above the reference energy level.

g_{oj} = probability or the statistical weight of the ground energy level ϵ_{oj} .

m_j = mass of a particle of the j species.

k = Boltzmann Constant.

h = Planck constant.

It was pointed out in Ref. 16 that g_{0j} are essentially the electronic partition functions for atoms and molecules and may be taken as constant for oxygen in the temperature range 1500°K to 8000°K.

Since atoms have only translational degrees of freedom,

$$f_1^{(r)} = f_1^{(v)} = 1 \quad (A5)$$

while for molecules in ground electronic energy state,

$$f_2^{(r)} = \frac{1}{2} \frac{T_t}{\Theta_r} \quad (A6)$$

where Θ_r is characteristic temperature for rotation; and according to the harmonic oscillator approximation where Θ_v is the characteristic temperature for vibration.

$$f_2^{(v)} = [1 - e^{-\Theta_v/T_v}]^{-1} \quad (A7)$$

From classical thermodynamics, the entropy of the mixture is (Ref. 29)

$$S = - \left[\left(\frac{\partial A_t}{\partial T_t} \right)_v + \left(\frac{\partial A_r}{\partial T_t} \right)_v + \left(\frac{\partial A_v}{\partial T_v} \right)_v \right] \quad (A8)$$

$$\left(\frac{\partial(A_t + A_r)}{\partial T_t} \right)_v = \frac{\partial}{\partial T_t} \left\{ -k T_t \sum N_j [\log f_j^{(t)} + \log f_j^{(r)} - \log N_j + 1] \right\} \quad (A9)$$

$$= -k \sum N_j [\log f_j^{(t)} + \log f_j^{(r)} - \log N_j + 1] - k T_t \left\{ \sum N_j \left(\frac{3}{2 T_t} + \frac{\epsilon_{0j}}{k T_t^2} \right) + \frac{N_2}{T_t} \right\} \quad (A10)$$

$$= -k \left\{ \sum N_j [\log f_j^{(t)} + \log f_j^{(r)} - \log N_j + \frac{5}{2}] + N_2 + \frac{N_1}{2} \frac{\Theta_D}{T_t} \right\}$$

where $\epsilon_{01} = \frac{1}{2} k \Theta_D$, $\epsilon_{02} = 0$, as given in Ref. 5, and Θ_D is the characteristic dissociation temperature. Now

$$\begin{aligned} \frac{\partial A_v}{\partial T_v} &= \frac{\partial}{\partial T_v} \left[k T_v N_2 \log (1 - e^{-\Theta_v/T_v}) \right] \\ &= k N_2 \log (1 - e^{-\Theta_v/T_v}) + k T_v N_2 \frac{-\frac{\Theta_v}{T_v^2} e^{-\Theta_v/T_v}}{1 - e^{-\Theta_v/T_v}} \\ &= k N_2 \left[\log (1 - e^{-\Theta_v/T_v}) - \frac{\Theta_v/T_v}{e^{\Theta_v/T_v} - 1} \right] \end{aligned} \quad (A11)$$

$$\text{Thus } S = k \left\{ N_1 \left[\log f_1^{(t)} - \log N_1 + \frac{5}{2} + \frac{1}{2} \frac{\Theta_D}{T_t} \right] + \left[\log f_2^{(t)} + \log f_2^{(r)} - \log N_2 + \frac{7}{2} \right] N_2 - N_2 \left[\log (1 - e^{-\Theta_v/T_v}) - \frac{\Theta_v/T_v}{e^{\Theta_v/T_v} - 1} \right] \right\} \quad (A12)$$

$$\left\{ \begin{aligned} N_1 k/pV &= 2\alpha R \\ N_2 k/pV &= (1-\alpha)R \end{aligned} \right. \quad (A13)$$

In terms of mass fractions

$$\left\{ \begin{aligned} N_1 k/pV &= 2\alpha R \\ N_2 k/pV &= (1-\alpha)R \end{aligned} \right. \quad (A14)$$

where α is the atomic mass fraction, R is the gas constant per unit mass of the diatomic gas. Thus for the specific entropy s of the mixture,

$$\begin{aligned}
 s &= \frac{S}{pV} = \frac{N_1 k}{pV} \left[\log \frac{f_1^{(1)}}{N_1} + \frac{5}{2} + \frac{1}{2} \frac{\theta_D}{T_t} \right] + \frac{N_2 k}{pV} \left[\log \frac{f_2^{(1)} f_2^{(2)}}{N_2} (1 - e^{-\theta_v/T_v})^{-1} + \frac{7}{2} + \frac{\theta_v/T_v}{e^{\theta_v/T_v} - 1} \right] \\
 &= 2\alpha R \left[\frac{5}{2} + \frac{1}{2} \frac{\theta_D}{T_t} + \log \frac{(2\pi m k T_t)^{3/2}}{h^3} \frac{V}{N_1} g_{01} e^{-\frac{\theta_D}{2T_t}} \right] \\
 &\quad + (1-\alpha) R \left[\frac{7}{2} + \frac{\theta_v/T_v}{e^{\theta_v/T_v} - 1} + \log \frac{1}{2} \frac{T_t}{\theta_n} (1 - e^{-\theta_v/T_v})^{-1} \frac{(4\pi m k T_t)^{3/2}}{h^3} \frac{V}{N_2} g_{02} \right] \\
 &= R \left\{ \frac{\alpha \theta_D}{T_t} + \frac{7+3\alpha}{2} + \frac{(1-\alpha)E_v}{T_v} + \log \left[g_{02} \frac{T_t}{\theta_n} (1 - e^{-\theta_v/T_v})^{-1} \frac{m}{p(1-\alpha)} \frac{(4\pi m k T_t)^{3/2}}{h^3} \right] \right\} \quad (A15) \\
 &\quad + \alpha \log \left[\frac{g_{01}^2 (2\pi m k T_t)^3}{h^6} \frac{m^2}{p^2 \alpha^2} e^{-\frac{\theta_D}{T_t}} \frac{m}{p(1-\alpha)} \frac{T_t}{\theta_n} g_{02} (1 - e^{-\theta_v/T_v})^{-1} \frac{(4\pi m k T_t)^{3/2}}{h^3} \right] \Bigg\} \\
 &= R \left\{ \frac{7+3\alpha}{2} + \frac{(1-\alpha)E_v}{T_v} + \frac{\alpha \theta_D}{T_t} + \log \left[g_{02} \frac{T_t}{\theta_n} (1 - e^{-\theta_v/T_v})^{-1} \frac{m}{p(1-\alpha)} \frac{(4\pi m k T_t)^{3/2}}{h^3} \right] \right. \\
 &\quad \left. + \alpha \log \left[\frac{g_{01}^2}{g_{02}} \frac{\theta_n}{T_t} (1 - e^{-\theta_v/T_v}) e^{-\frac{\theta_D}{T_t}} \frac{(1-\alpha)m}{p\alpha^2} \frac{(\pi m k T_t)^{3/2}}{h^3} \right] \right\}
 \end{aligned}$$

In terms of the characteristic dissociation density p_D and reference entropy s_n , defined by

$$p_D = \frac{g_{01}^2}{g_{02}} \frac{(\pi m k)^{3/2}}{h^3} m \frac{\theta_v^{3/2} \theta_n}{2} \quad (A16)$$

and

$$s_n = R \log \left[p e^{\frac{7}{2}} \left(\frac{g_{02}}{g_{01}} \right)^2 \left(\frac{T_n}{\theta_n} \right)^2 \right] \quad (A17)$$

where T_n is a reference temperature, the expression for the specific entropy Eq. (A15) can be reduced to

$$\begin{aligned}
 \frac{s - s_n}{R} &= \frac{3\alpha}{2} + \frac{(1-\alpha)E_v}{T_v} + (1+\alpha) \frac{\theta_D}{T_t} + 2 \log \left[\frac{T_t}{\theta_n} \frac{\alpha}{(1-\alpha)(1 - e^{-\theta_v/T_v})} \right] \\
 &\quad + (1+\alpha) \log \left[\frac{2p_D}{p} \left(\frac{T_t}{\theta_v} \right)^{\frac{1}{2}} (1 - e^{-\theta_v/T_v}) e^{-\frac{\theta_D}{T_t}} \frac{(1-\alpha)}{\alpha^2} \right] \quad (A18)
 \end{aligned}$$

The internal energy can be written as

$$E = \frac{\partial}{\partial (\frac{1}{T_t})} \left(\frac{A_t + A_n}{T_t} \right) + \frac{\partial}{\partial (\frac{1}{T_v})} \left(\frac{A_v}{T_v} \right) \quad (A19)$$

$$\begin{aligned}
 \frac{\partial}{\partial (\frac{1}{T_t})} \left(\frac{A_t + A_n}{T_t} \right) &= k T_t^2 \frac{\partial}{\partial T_t} \left\{ N_1 \log f_1^{(1)} + N_2 \log f_2^{(1)} f_2^{(2)} \right\} \\
 &= k T_t^2 \left\{ N_1 \left(\frac{3}{2T_t} + \frac{\theta_D}{2T_t^2} \right) + N_2 \left(\frac{3}{2T_t} + \frac{1}{T_t} \right) \right\} \quad (A20)
 \end{aligned}$$

$$\begin{aligned}
\frac{\partial}{\partial (\frac{\theta_v}{T_v})} \left(\frac{A_v}{T_v} \right) &= k T_v^2 \frac{\partial}{\partial T_v} \left[N_2 \log (1 - e^{-\theta_v/T_v})^{-1} \right] \\
&= -k T_v^2 N_2 \frac{1}{1 - e^{-\theta_v/T_v}} (-e^{-\theta_v/T_v}) \left(\frac{\theta_v}{T_v^2} \right) \\
&= k N_2 \frac{\theta_v}{e^{\theta_v/T_v} - 1}
\end{aligned} \tag{A21}$$

The specific internal energy is

$$\begin{aligned}
e = \frac{E}{pV} &= \frac{k}{pV} \left[N_1 \left(\frac{3}{2} T_t + \frac{\theta_D}{2} \right) + \frac{5}{2} N_2 T_t + N_2 \frac{\theta_v}{e^{\theta_v/T_v} - 1} \right] \\
&= \frac{k N_1}{pV} \left(\frac{3}{2} T_t + \frac{\theta_D}{2} \right) + \frac{k N_2}{pV} \left(\frac{5}{2} T_t + \frac{\theta_v}{e^{\theta_v/T_v} - 1} \right)
\end{aligned}$$

or with the aid of Eqs. (A13), (A14),

$$\begin{aligned}
&= 2\alpha R \left(\frac{3}{2} T_t + \frac{\theta_D}{2} \right) + (1-\alpha) R \left(\frac{5}{2} T_t + \frac{\theta_v}{e^{\theta_v/T_v} - 1} \right) \\
&= R \left[\left(3\alpha + \frac{5}{2} - \frac{5\alpha}{2} \right) T_t + (1-\alpha) \frac{\theta_v}{e^{\theta_v/T_v} - 1} + \alpha \theta_D \right] \\
&= R \left[\frac{5+\alpha}{2} T_t + (1-\alpha) \frac{\theta_v}{e^{\theta_v/T_v} - 1} + \alpha \theta_D \right]
\end{aligned} \tag{A22}$$

The pressure is given by (Ref. 29)

$$\begin{aligned}
p &= - \left(\frac{\partial A}{\partial V} \right) = - \frac{\partial}{\partial V} (A_t + A_h + A_v) \\
&= - \frac{\partial}{\partial V} \left\{ -k T_t \left[N_1 \log f_1^{(t)} + N_2 \log f_2^{(t)} \right] \right\} \\
&= k T_t \left[\frac{N_1 + N_2}{V} \right]
\end{aligned}$$

or with the aid of Eqs. (A13), (A14),

$$\begin{aligned}
&= k T_t \left[\frac{2\alpha p R}{k} + \frac{(1-\alpha) p R}{k} \right] \\
&= p R (1+\alpha) T_t
\end{aligned} \tag{A23}$$

The chemical potentials are (Ref. 29)

$$\mu_i = \frac{\partial A_i}{\partial N_i} = \frac{\partial}{\partial N_i} (A_t + A_h + A_v) \tag{A24}$$

Thus the chemical potential for the atoms is

$$\begin{aligned}
 \mu_1 &= \frac{\partial(A)}{\partial N_1} = \frac{\partial}{\partial N_1} (A_t + A_n + A_v) \\
 &= \frac{\partial}{\partial N_1} \left\{ -kT_t \left[N_1 (\log f_1^{(t)} - \log N_1 + 1) + N_2 (\log f_2^{(n)} f_2^{(t)} - \log N_2 + 1) \right] \right. \\
 &\quad \left. - kT_v N_2 \log f_2^{(v)} \right\} \\
 &= -kT_t \left\{ (\log f_1^{(t)} - \log N_1 + 1) - 1 \right\} \\
 &= -kT_t \log \frac{f_1^{(t)}}{N_1} \\
 &= -kT_t \log \left[\frac{(2\pi m k T_t)^{3/2}}{h^3} \cdot \frac{V}{N_1} g_{01} e^{-\frac{\theta_D}{2T_t}} \right] \\
 &= -kT_t \log \left[\frac{(2\pi m k T_t)^{3/2}}{h^3} g_{01} e^{-\frac{\theta_D}{2T_t}} \frac{m}{\rho \alpha} \right] \\
 &= \frac{1}{2} k \theta_D - kT_t \log \left[\frac{(2\pi m k)^{3/2}}{h^3} g_{01} \frac{m}{\rho \alpha} T_t^{3/2} \right]
 \end{aligned} \tag{A25}$$

For the molecule, the chemical potential is

$$\begin{aligned}
 \mu_2 &= \frac{\partial}{\partial N_2} \left\{ -kT_t N_2 (\log f_2^{(t)} f_2^{(n)} - \log N_2 + 1) - kT_v N_2 \log f_2^{(v)} \right\} \\
 &= -kT_t \left(\log \frac{f_2^{(t)} f_2^{(n)}}{N_2} + 1 - 1 \right) - kT_v \log f_2^{(v)} \\
 &= -kT_t \log \left[\frac{(4\pi m k T_t)^{3/2}}{h^3} \cdot \frac{V}{N_2} g_{02} \frac{1}{2} \frac{T_t}{\theta_n} \right] - kT_v \log (1 - e^{-\theta_v/T_v})^{-1} \\
 &= -kT_t \log \left[\frac{(4\pi m k)^{3/2}}{h^3} \cdot g_{02} \frac{m_1 T_t^{5/2}}{\rho (1-\alpha) 2 \theta_n} \right] - kT_v \log (1 - e^{-\theta_v/T_v})^{-1}
 \end{aligned} \tag{A26}$$

The specific chemical potentials g_1 and g_2 for atoms and molecules respectively are

$$g_1 = \frac{\mu_1}{m} = R \theta_D - RT_t \log \left(\frac{K_1 T_t^{3/2}}{\rho \alpha} \right) \tag{A27}$$

$$g_2 = \frac{\mu_2}{2m} = -RT_t \log \left[K_2 \frac{T_t^{5/2}}{\rho (1-\alpha)} \right] - RT_v \log (1 - e^{-\theta_v/T_v})^{-1} \tag{A28}$$

where

$$K_1 = g_{01} \frac{(2\pi k)^{3/2}}{h^3} m^{5/2} \quad (A29)$$

$$K_2 = g_{02} \frac{(4\pi k)^{3/2}}{h^3} \frac{m^{5/2}}{\theta_n} \quad (A30)$$

The specific enthalpy h is

$$\begin{aligned} h &= \frac{H}{pV} = \frac{E + pV}{pV} = e + p/p \\ &= R \left[\frac{7+3\alpha}{2} T_t + (1-\alpha) \frac{\theta_v}{e^{\theta_v/T_v} - 1} + \alpha \theta_D \right] \end{aligned} \quad (A31)$$

from Eqs. (A22) and (A23)

For vibrational and dissociational equilibrium, one has the condition that the specific chemical potentials of atoms and molecules be equal for a pure diatomic gas.

i. e.

$$g_1 = g_2 \quad (A32)$$

$$T_t = T_v = T \quad (A33)$$

Then from Eqs. (A27), (A28), it can be shown that

$$\frac{\alpha e^2}{1-\alpha e} = \frac{2p_D}{p} \left(\frac{T}{\theta_v} \right)^{1/2} (1 - e^{-\theta_v/T}) e^{-\theta_D/T} \quad (A34)$$

where αe is the equilibrium value of α . For thermal and dissociational equilibrium, the last term in Eq. (A18) for entropy vanishes by virtue of Eq. (A34), giving a relation between αe and T in terms of entropy which can be derived in a slightly different fashion starting from differential flow relations and Eq. (A34) for complete equilibrium flow. (See Appendix C)

This relation is

$$\frac{3\alpha}{2} + \frac{(1-\alpha)\theta_v}{T} + (1+\alpha)\frac{\theta_D}{T} + 2 \log \left[\frac{T_t \alpha}{T_n (1-\alpha)(1-e^{-\theta_v/T})} \right] - \frac{s-s_n}{R} = \text{constant} \quad (A35)$$

Entropy Equation

Eq. (A18) may be differentiated to yield an equation for entropy change in

vibrational and dissociational nonequilibrium in terms of $d\mathcal{E}_v$, $d\alpha$, dT_t , dP as follows:-

$$\begin{aligned}
 \frac{dS}{R} &= \frac{3}{2} d\alpha - \frac{\mathcal{E}_v}{T_v} d\alpha + (1-\alpha) \left(\frac{d\mathcal{E}_v}{T_v} - \frac{\mathcal{E}_v}{T_v^2} dT_v \right) + d\alpha \frac{\theta_D}{T_t} - \frac{(1+\alpha)\theta_D}{T_t^2} dT_t \\
 &\quad + 2 \frac{dT_t}{T_t} + \frac{2d\alpha}{\alpha} + \frac{2d\alpha}{1-\alpha} - \frac{2}{1-e^{-\theta_v/T_v}} (-e^{-\theta_v/T_v}) \left(\frac{\theta_v}{T_v^2} \right) dT_v \\
 &\quad + d\alpha \log \left[\frac{2P}{P} \left(\frac{T_t}{\theta_D} \right)^{\frac{1}{2}} (1-e^{-\theta_v/T_v}) e^{-\theta_D/T_t} \frac{(1-\alpha)}{\alpha^2} \right] \\
 &\quad + (1+\alpha) \left[-\frac{dP}{P} + \frac{1}{2T_t} dT_t + \frac{1}{1-e^{-\theta_v/T_v}} (-e^{-\theta_v/T_v}) \left(\frac{\theta_v}{T_v^2} \right) dT_v \right. \\
 &\quad \left. + \frac{\theta_D}{T_t^2} dT_t - \frac{d\alpha}{1-\alpha} - \frac{2d\alpha}{\alpha} \right] \\
 &= d\alpha \left\{ \frac{3}{2} - \frac{\mathcal{E}_v}{T_v} + \frac{\theta_D}{T_t} + \frac{2}{\alpha} + \frac{2}{1-\alpha} - \frac{1+\alpha}{1-\alpha} - \frac{2(1+\alpha)}{\alpha} \right. \\
 &\quad \left. + \log \left[\frac{2P}{P} \left(\frac{T_t}{\theta_D} \right)^{\frac{1}{2}} (1-e^{-\theta_v/T_v}) e^{-\theta_D/T_t} \frac{(1-\alpha)}{\alpha^2} \right] \right\} \quad (A36) \\
 &\quad + dT_t \left\{ -\frac{(1+\alpha)\theta_D}{T_t^2} + \frac{2}{T_t} + \frac{1+\alpha}{2T_t} + \frac{\theta_D}{T_t^2} \right\} - (1+\alpha) \frac{dP}{P} \\
 &\quad + d\mathcal{E}_v \left\{ (1-\alpha) \left[\frac{1}{T_v} - \frac{\mathcal{E}_v}{T_v^2} \frac{dT_v}{d\mathcal{E}_v} \right] + \frac{2\mathcal{E}_v}{T_v^2} \frac{dT_v}{d\theta_v} - (1+\alpha) \frac{\mathcal{E}_v}{T_v^2} \frac{dT_v}{d\mathcal{E}_v} \right\} \\
 \therefore \frac{dS}{R} &= d\alpha \left\{ \frac{1}{2} - \frac{\mathcal{E}_v}{T_v} + \frac{\theta_D}{T_t} + \log \left[\frac{2P}{P} \left(\frac{T_t}{\theta_D} \right)^{\frac{1}{2}} (1-e^{-\theta_v/T_v}) e^{-\theta_D/T_t} \frac{(1-\alpha)}{\alpha^2} \right] \right\} \\
 &\quad - (1+\alpha) \frac{dP}{P} + \frac{dT_t}{T_t} \left(\frac{5+\alpha}{2} - \frac{\alpha\theta_D}{T_t} \right) + \frac{(1-\alpha) d\mathcal{E}_v}{T_v}
 \end{aligned}$$

which is the same as given in Ref. 16.

APPENDIX B

Derivation of the Rate Equations

The exact equation for the net rate of change of molecules in the vibrational energy level j with energy E_j is (Eq. (80))

$$\begin{aligned} \frac{d[A_j]}{dt} = & -k_{j,0}[A_j][A_2] + k_{0,j}[A_0][A_2] - k_{j,1}^a[A_j][A] + \\ & k_{1,j}^a[A_1][A] - k_{d,j}[A_j][x] + k_{r,j}[A]^2[x] \end{aligned} \quad (80)$$

which under the assumptions given in Section 3.3 simplifies to

$$\begin{aligned} \frac{d[A_j]}{dt} = & -k_{j,j-1}[A_j][A_2] - k_{j,j+1}[A_j][A_2] + k_{j-1,j}[A_{j-1}][A_2] \\ & + k_{j+1,j}[A_{j+1}][A_2] - k_{d,j}[A_j][x] + k_{r,j}[A]^2[x] \\ = & -k_{1,0}[A_2] \left\{ j[A_j] - (j+1)[A_{j+1}] + \exp\left(-\frac{h\nu}{kT}\right) [(j+1)[A_j] - j[A_{j-1}]] \right\} \\ & - k_{d,j}[A_j][x] + k_{r,j}[A]^2[x] \end{aligned} \quad (B1)$$

where the relations (70), (71) between $k_{j,j-1}$ and $k_{j,j+1}$ are used.

Dissociational Rate Equation

The dissociation rate equation is obtained by taking the sum of equations of type (B1) for all the vibrational energy levels, namely

$$\begin{aligned} \frac{d[A_2]}{dt} = \sum_j \frac{d[A_j]}{dt} = & -k_{1,0}[A_2] \sum_j \left\{ j[A_j] - (j+1)[A_{j+1}] \right. \\ & \left. + \exp\left(-\frac{h\nu}{kT}\right) [(j+1)[A_j] - j[A_{j-1}]] \right\} - [x] \sum_j k_{d,j}[A_j] + \sum_j k_{r,j}[A]^2[x] \end{aligned} \quad (B2)$$

It may be shown that the sum in the first bracket in Eq. (B2) is zero as follows:-

For level $(j+1)$ and $(j-1)$, the first bracket in Eq. (B2) is

$$(j+1)[A_{j+1}] - (j+2)[A_{j+2}] + \exp\left(-\frac{h\nu}{kT}\right) [(j+2)[A_{j+1}] - (j+1)[A_j]] \quad (B3)$$

$$(j-1)[A_{j-1}] - j[A_j] + \exp\left(-\frac{h\nu}{kT}\right) [j[A_{j-1}] - (j-1)[A_{j-2}]] \quad (B4)$$

Adding (B3), (B4) with

$$j[A_j] - (j+1)[A_{j+1}] + \exp\left(-\frac{h\nu}{kT}\right) \left[(j+1)[A_j] - j[A_{j-1}] \right] \quad (B5)$$

gives

$$(j-1)[A_{j-1}] - (j+2)[A_{j+2}] + \exp\left(-\frac{h\nu}{kT}\right) \left[(j+1)[A_{j+1}] - (j-1)[A_{j-2}] \right] \quad (B6)$$

Let $j=0$ be the ground level and $j=l$ the last level. Then for $j=0$, the expression in the first bracket of (B2) is

$$0[A_0] - (0+1)[A_{0+1}] + \exp\left(-\frac{h\nu}{kT}\right) \left[(0+1)[A_0] - 0[A_{0-1}] \right] \quad (B7)$$

or

$$-A_1 + \exp\left(-\frac{h\nu}{kT}\right) [A_0]$$

while for $j=l$,

$$l[A_l] - (l+1)[A_{l+1}] + \exp\left(-\frac{h\nu}{kT}\right) \left[(l+1)[A_l] - l[A_{l-1}] \right] \quad (B8)$$

But the term $\exp\left(-\frac{h\nu}{kT}\right) (l+1)[A_l]$ is due to the molecules lost to level $(l+1)$. As the number of levels is only l , this term should be zero. So also $[A_{l+1}] = 0$. Thus for level $j=l$, one has

$$l[A_l] - l \exp\left(-\frac{h\nu}{kT}\right) [A_{l-1}] \quad (B9)$$

But the negative of the sum of (B7) and (B9) will be the net result of summation over the levels $j=l$, to $j=1-l$.

Thus

$$\frac{d[A_2]}{dt} = \sum_j \frac{d[A_j]}{dt} = -[X] \sum k_{dj} [A_j] + [A]^2 [X] \sum k_{nj} \quad (B10)$$

$$= -\sum Z_{dj} + \sum Z_{nj} \quad (B11)$$

where Z_{dj} and Z_{nj} dissociational and recombinational rates for level j . Under the assumptions of Section 3.3 and specialising for collisions with molecules only (i.e. replacing $[X]$ by $[A_2]$).

$$\sum Z_{nj} = [A]^2 [A_2] \sum k_{nj} = k_n [A]^2 [A_2] \quad (B12)$$

while

$$[A_2] \sum k_{dj} [A_j] = \sum Z_{dj} = Z_0 \sum c P_j N_j N_2 M (D - E_j) \quad (B13)$$

where Z_0 is the total number of collisions per cc per sec per unit concentrations, c is a constant, $[A_2] = N_2$ is the concentration of the total number of molecules, $[A_j] = N_j$ is the concentration of the number of molecules in vibrational level j , $P_j = e^{-(D-E_j)/kT}$ is the probability or effi-

ciency for dissociation from level j , and $M(D-E_j)$ is the fractional number of collisions with energy greater than $D-E_j$. $M(D-E_j)$ may be written from statistical mechanics as

$$M(D-E_j) = e^{-(D-E_j)/kT_t} \quad (B14)$$

where T_t is the translational temperature and D is the dissociational energy of the molecules. In terms of an overall rate coefficient k_d ,

$$[A_2] \sum k_{dj}^m [A_j] = \sum Z_{dj} = k_d^m [A_2]^2 = k_d^m N_2^2 \quad (B15)$$

From Eqs. (B13), (B15)

$$\begin{aligned} \sum Z_{dj} &= Z_0 \sum c p_j N_j N_2 M(D-E_j) \\ &= k_d^m N_2^2 \end{aligned} \quad (B16)$$

or

$$\begin{aligned} k_d^m &= Z_0 \sum c p_j \frac{N_j}{N_2} M(D-E_j) \\ &= Z_0 c \sum e^{-(D-E_j)/kU} \frac{N_j}{N_2} e^{-(D-E_j)/kT_t} \end{aligned} \quad (B17)$$

Under the assumption of Boltzmann distribution in vibration at a temperature T_v ,

$$\frac{N_j}{N_2} = \frac{e^{-E_j/kT_v}}{\sum e^{-E_j/kT_v}} \quad (B18)$$

Thus

$$k_d^m = Z_0 c \sum e^{-(D-E_j)/kU} \frac{e^{-E_j/kT_v}}{\sum e^{-E_j/kT_v}} e^{-(D-E_j)/kT_t} \quad (B19)$$

For the case of vibrational equilibrium with translation, $T_v = T_t$ and

$$k_{deg} = Z_0 c \sum e^{-(D-E_j)/kU} \frac{e^{-E_j/kT_t}}{\sum e^{-E_j/kT_t}} e^{-(D-E_j)/kT_t} \quad (B20)$$

Dividing Eq. (B19) by (B20) and denoting the expressions containing the summation of exponentials by Q i. e.

$$Q(T) = \sum e^{-E_j/kT} \quad (B21)$$

one obtains

$$\begin{aligned} V = \frac{k_d}{k_{deg}} &= \frac{Z_0 c \sum e^{-(D-E_j)/kU} e^{-E_j/kT_v} e^{-(D-E_j)/kT_t} / Q(T_v)}{Z_0 c \sum e^{-(D-E_j)/kU} e^{-E_j/kT_t} e^{-(D-E_j)/kT_t} / Q(T_t)} \\ &= \frac{Q(T_t)}{Q(T_v)} \cdot \frac{e^{-D/kU} e^{-D/kT_t} \sum e^{-E_j/k(\frac{1}{T_v} - \frac{1}{T_t} - \frac{1}{U})}}{e^{-D/kU} e^{-D/kT_t} \sum e^{-E_j/k(\frac{1}{T_t} - \frac{1}{T_t} - \frac{1}{U})}} \\ &= \frac{Q(T_t)}{Q(T_v)} \cdot \frac{Q(T_t)}{Q(-U)} \end{aligned} \quad (B22)$$

where

$$\frac{1}{T_f} = \frac{1}{T_v} - \frac{1}{T_t} - \frac{1}{U} \quad (B23)$$

Thus the rate equation (B11) reduces to

$$\begin{aligned}
 \frac{d[A_2]}{dt} &= -k_d[A_2]^2 + k_n[A]^2[A_2] \\
 &= -V k_{deg} [A_2]^2 + k_n [A]^2 [A_2] \\
 &= -k_n [A]^2 [A_2] \left\{ V K_C \frac{[A_2]}{[A]^2} - 1 \right\}
 \end{aligned} \tag{B24}$$

where K_C is the equilibrium constant

$$K_C = \frac{k_{deg}}{k_n} \tag{B25}$$

Let the atomic mass fraction be α ,

$$\alpha = \frac{\rho_i}{\rho} \tag{B26}$$

where ρ_i is the partial density of atoms and ρ is the total density, $[A_2]$ and $[A]$ may be shown to be (see Ref. 5).

$$N_1 = [A] = \frac{\rho \alpha}{m_a} \quad \text{mole/cm}^3 \tag{B27}$$

$$N_2 = [A_2] = \frac{\rho(1-\alpha)}{2m_a} \quad \text{mole/cm}^3 \tag{B28}$$

where m_a is the mass of one mole of atoms and

$$m_a = m N_A \quad \text{gm mole} \tag{B29}$$

where N_A is Avogadro's number and m is the mass of an atom. Since the total number of atoms is constant,

$$2[A_2] + [A] = \text{constant} \tag{B30}$$

Differentiating

$$2 \frac{d[A_2]}{dt} + \frac{d[A]}{dt} = 0$$

or

$$\frac{d[A]}{dt} = -2 \frac{d[A_2]}{dt} \tag{B31}$$

$$\begin{aligned}
 \text{Thus } \frac{d[A]}{dt} &= \frac{d(\rho \alpha / m_a)}{dt} = -2 \frac{d[A_2]}{dt} = 2 k_n [A]^2 [A_2] \left\{ V K_C \frac{[A_2]}{[A]^2} - 1 \right\}
 \end{aligned} \tag{B32}$$

$$\text{or } \frac{d(P\alpha/m_a)}{dt} = 2k_n \frac{P^2 \alpha^2}{m_a^2} \cdot \frac{P(1-\alpha)}{2m_a} \left\{ V K_c \frac{P(1-\alpha) m_a}{P^2 \alpha^2 / m_a^2} - 1 \right\}$$

$$\frac{d(P\alpha)}{dt} = \frac{k_n P^3}{m_a^2} \cdot \alpha^2 (1-\alpha) \left\{ \frac{V K_c m_a}{2P} \frac{(1-\alpha)}{\alpha^2} - 1 \right\} \quad (\text{B32})$$

Eq. (B32) is taking into account only the molecule-molecule collisions. For the atom molecule collisions, from the assumption $k_{da} = \lambda k_{dm}$

$$\begin{aligned} \frac{d[A_2]}{dt} &= -k_{da} [A_2][A] + k_{na} [A]^3 \\ &= -k_{na} [A]^3 \left\{ V K_c \frac{[A_2]}{[A]^2} - 1 \right\} \\ &= -\lambda k_n [A]^3 \left\{ V K_c \frac{[A_2]}{[A]^2} - 1 \right\} \\ &= -\lambda k_n \frac{P^3 \alpha^3}{m_a^3} \left\{ V K_c \frac{m_a}{2P} \frac{(1-\alpha)}{\alpha^2} - 1 \right\} \\ \frac{d[A]}{dt} &= \frac{d(P\alpha/m_a)}{dt} = -2 \frac{d[A_2]}{dt} = \frac{2\lambda k_n P^3 \alpha^3}{m_a^3} \left\{ V K_c \frac{m_a}{2P} \frac{(1-\alpha)}{\alpha^2} - 1 \right\} \end{aligned} \quad (\text{B33})$$

$$\frac{d(P\alpha)}{dt} = \frac{2\lambda k_n P^3 \alpha^3}{m_a^2} \left\{ V K_c \frac{m_a}{2P} \frac{(1-\alpha)}{\alpha^2} - 1 \right\} \quad (\text{B34})$$

Adding Eqs. (B32) and (B34), the net rate of mass production of atoms is

$$\frac{d(P\alpha)}{dt} = \frac{k_n P^3}{m_a^2} \alpha^2 (1-\alpha + 2\lambda\alpha) \left\{ V K_c \frac{m_a}{2P} \frac{(1-\alpha)}{\alpha^2} - 1 \right\} \quad (\text{B35})$$

$$= P \psi (VL - 1) \quad (\text{B36})$$

where $\psi = \frac{k_n P^2 \alpha^2 (1-\alpha + 2\lambda\alpha)}{m_a^2} \quad (\text{B37})$

$$L = \frac{m_a K_c}{2P} \frac{(1-\alpha)}{\alpha^2} \quad (\text{B38})$$

By the use of species continuity equation, one finally gets

$$\frac{d\alpha}{dt} = \psi (VL - 1) \quad (\text{B39})$$

Vibrational Rate Equation

The vibrational rate equation is obtained by multiplying Eq. (B1) by the vibrational energy E_j for level j and summing over all the energy levels, i. e.

$$\frac{dE_v}{dt} = \sum E_j \frac{d[A_j]}{dt} = -k_{10} [A_2] \sum E_j \{ j [A_j] - (j+1) [A_{j+1}] + \alpha \left(1 - \frac{h\nu}{kT} \right) [A_0] \} + [X] \sum E_j k_d [A_j] + [A] [X] \sum k_{vj} E_j \quad (B40)$$

Consider first the dissociation term for molecule-molecule collisions,

$$[A_2] \sum E_j k_d [A_j] = \sum Z_d E_j = \bar{E}_1 N_2^2 \quad (B41)$$

where \bar{E}_1 is the average energy lost per mole (N_2 is the number of moles per cc),

$$\begin{aligned} \bar{E}_1 &= \frac{\sum Z_d E_j}{N_2^2} = Z_0 c \sum P_j \frac{N_j}{N_2} M (D - E_j) E_j \\ &= Z_0 c \sum e^{-(D-E_j)/kT_0} e^{-E_j/kT_0} e^{-(D-E_j)/kT_t} E_j / Q(T_0) \\ &= c Z_0 e^{-D/kT_0} e^{-D/kT_t} \sum E_j e^{-E_j/kT_t} / Q(T_0) \end{aligned} \quad (B42)$$

where T_t is defined in Eq. (B23). From Eq. (B19)

$$c Z_0 \frac{e^{-D/kT_0} e^{-D/kT_t}}{Q(T_0)} = \frac{k_d}{Q(T_f)} \quad (B43)$$

which when substituted in Eq. (B42) gives

$$\begin{aligned} \bar{E}_1 &= \frac{k_d}{Q(T_f)} \sum E_j e^{-E_j/kT_f} \\ &= k_d \mathcal{E}(T_f) \end{aligned} \quad (B44)$$

where $\mathcal{E}(T_f)$ is defined as

$$\bar{E} = \mathcal{E}(T_f) = \frac{\sum E_j e^{-E_j/kT_f}}{Q(T_f)} \quad (B45)$$

From the assumption of $k_{da} = \lambda k_{dm}$, the \bar{E} for atom-molecule collision is

$$\bar{E}_2 = \lambda k_d \mathcal{E}(T_f) \quad (B46)$$

Thus for the complete dissociation term,

$$\begin{aligned}
 [x] \sum E_j k_{dj} [A_j] &= \bar{E}_1 N_2^2 + \bar{E}_2 N_2 N_1 \\
 &= N_2 [N_2 k_d \varepsilon(T_f) + N_1 \lambda k_d \varepsilon(T_f)] \\
 &= N_2 k_d \varepsilon(T_f) (N_2 + \lambda N_1) \\
 &= N_2 k_d (N_2 + N_1 \lambda) \varepsilon(T_f) \\
 &= N_2 k_d (N_2 + \lambda N_1) \bar{E} \\
 &= k_d \frac{p(1-\alpha)}{2m_a} \cdot \frac{p}{2m_a} (1-\alpha + 2\lambda\alpha) \bar{E} \\
 &= k_d \frac{p^2(1-\alpha)}{4m_a^2} (1-\alpha + 2\lambda\alpha) \bar{E}
 \end{aligned} \tag{B47}$$

For the recombination term for atom-molecule collisions

$$\begin{aligned}
 [A]^2 [A_2] \sum k_{nj} E_j &= \bar{G}_1 [A]^2 [A_2] \\
 \bar{G}_1 &= k_n (\sum k_{nj} E_j / k_n)
 \end{aligned}$$

Now k_n and k_{nj} can be written in terms of K_c , k_{deg} and $k_{dj'eg}$ as (See Eq. (B89),

$$\begin{aligned}
 k_n &= \frac{k_{deg}}{K_c} \\
 k_{nj} &= \frac{k_{dj'eg}}{K_c} \left(\frac{[A_j]}{[A_2]} \right)_{eg}
 \end{aligned}$$

From Eq. (B20)

$$k_{deg} = c Z_0 e^{-D/kU} e^{-D/kT_t} \frac{Q(-U)}{Q(T_t)} \tag{B20}$$

From Eq. (B90),

$$k_{dj'eg} = \left(\frac{[A_j]}{[A_2]_{eg}} \right) k_{dj'eg} = c Z_0 e^{-D/kU} e^{-D/kT_t} e^{E_j/kU} / Q(T_t) \tag{B48}$$

so

$$\bar{G}_1 = k_n \left(\sum \frac{k_{dj'eg} E_j}{k_{deg}} \right) = k_n \left(\frac{\sum E_j e^{E_j/kU}}{Q(-U)} \right) = k_n \varepsilon(-v)$$

For molecule-molecule collisions, under the assumption $k_{na} = \lambda k_n$,

$$\begin{aligned} [A]^3 \sum k_{nj} E_j &= [A]^3 \bar{G} \\ &= \lambda k_n [A]^3 \varepsilon(-U) \end{aligned} \quad (B49)$$

For the complete recombination term

$$\begin{aligned} [A]^2 [x] \sum k_{nj} E_j &= \bar{G}_1 [A]^2 [A_2] + \bar{G}_2 [A]^3 \\ &= k_n [A]^2 \{ [A_2] + \lambda [A] \} \varepsilon(-U) \\ &= k_n \frac{p^2 \alpha^2}{m_a^2} \frac{p}{2m_a} (1 - \alpha + 2\lambda \alpha) \bar{G} \end{aligned} \quad (B50)$$

where

$$\bar{G} = \varepsilon(-U) = \frac{\sum E_j e^{E_j/kU}}{Q(-U)} \quad (B51)$$

The remaining terms in Eq. (B40) are due to internal changes of the number of molecules in each vibrational level and these terms are reduced to the form

$$(E_\infty - E_v) / \tau_v \quad (B52)$$

where E_∞ is the vibrational energy calculated at the local translation temperature by the Landau-Teller model. Thus the vibrational relaxation equation is given finally in the form

$$\frac{dE_v}{dt} = \frac{E_\infty - E_v}{\tau_v} - k_d \frac{p^2 (1-\alpha)}{4m_a^2} (1 - \alpha + 2\lambda \alpha) \bar{E} + k_n \frac{p^2 \alpha^2}{2m_a^2} (1 - \alpha + 2\lambda \alpha) \bar{G} \quad (B53)$$

From Eqs. (B35)-(B38), it will be seen that the coefficients of the second and third terms in Eq. (B53) are simply $\frac{p^2 \gamma V L}{2m_a}$ and $\frac{p^2 \gamma}{2m_a}$ respectively. Thus

$$\frac{dE_v}{dt} = \frac{E_\infty - E_v}{\tau_v} - \frac{p^2 \gamma V L}{2m_a} \bar{E} + \frac{p^2 \gamma}{2m_a} \bar{G} \quad (B54)$$

It may be noted that the vibrational energy E_v in the above is the total vibrational energy for N_2 moles/cc

$$E_v = \sum N_j E_j = N_2 N_A \varepsilon_v \quad (B55)$$

where ε_v is the specific vibrational energy, and N_A is Avogadro's

number. Since Σ_v is used in the total energy equation, Eq. (B54) may be written for Σ_v as follows:-

$$\frac{dE_v}{dt} = \frac{d}{dt} (N_2 N_A E_v) = (N_2 \frac{dE_v}{dt} + E_v \frac{dN_2}{dt}) N_A \quad (B56)$$

From equation (B31) $\frac{dN_2}{dt} = \frac{dPA_2}{dt} = -\rho \gamma (VL-1)/2m_a$
and from Eq. (B28), $N_2 = \rho(1-\alpha)/2m_a$, thus

$$\begin{aligned} \frac{dE_v}{dt} &= \frac{1}{N_2} \left(\frac{1}{N_A} \frac{dE_v}{dt} - E_v \frac{dN_2}{dt} \right) \\ &= \frac{\frac{E_a}{N_A N_2} - \frac{E_v}{N_A N_2}}{T_v} - \frac{2m_a}{\rho(1-\alpha)} \left[\frac{\rho \gamma VL \bar{E}}{m_a N_A} - \frac{\rho \gamma \bar{G}}{2m_a N_A} \right] \\ &\quad + E_v \frac{2m_a}{\rho(1-\alpha)} \cdot \frac{\rho \gamma (VL-1)}{2m_a} \end{aligned} \quad (B57)$$

or

$$\frac{dE_v}{dt} = \frac{E_a - E_v}{T_v} - \frac{\gamma VL(\bar{E} - E_v)}{(1-\alpha)} + \frac{\gamma}{1-\alpha} (\bar{G} - E_v)$$

where now \bar{E} and \bar{G} are specific energies.

Determination of the Parameter U

In the collision model for chemical reaction of diatomic molecules, a parameter U with the dimensions of temperature is introduced to describe the efficiency or probability of dissociation from a given level by writing this efficiency as

$$p_j = e^{-(D-E_j)/kU} \quad (B58)$$

It is implicitly assumed here that the parameter U is independent of the vibrational level. Under the most general circumstances of nonequilibrium between vibration and translation i.e. for a non-Boltzmann distribution in vibrational energy, U has to be taken as a function of the level j or its vibrational energy E_j and the translational temperature T_t i.e.

$$U_j = U_j(E_j, T_t) \quad (B59)$$

If the dissociational rates from different energy levels are known independently, then U_j can be evaluated from the relation between p_j and k_{dj} namely,

$$\begin{aligned} k_{dj} &= \frac{Z_{dj}}{N_j N_2} = c Z_0 p_j M(D-E_j) \\ &= c Z_0 e^{-(D-E_j)/kU_j} e^{-(D-E_j)/kT_t} \end{aligned} \quad (B60)$$

which can be solved for U_j knowing k_d and T_t . For a less complex case of Boltzmann distribution in vibration, if one knows k_d for vibrational nonequilibrium, one can calculate U as a function of T_t and T_v i. e. $U(T_t, T_v)$ from the relation

$$k_d = \sum c Z_0 e^{-(D-E_j)/kU} \frac{N_j}{N_2} e^{-(D-E_j)/kT_t} \quad (B61)$$

where k_d and T_t are known and N_j may be expressed in terms of the vibrational temperature T_v as

$$N_j/N_2 = e^{-E_j/kT_v} / Q(T_v) \quad (B62)$$

Since little experimental data is available even for k_d only the simplest case of U being a function of T_t can be determined. This can be done as follows. Writing the expression for k_d in the case for which vibration and translation are in equilibrium, namely,

$$[k_{deg}]_{\text{theo}} = c Z_0 \sum e^{-(D-E_j)/kU} \frac{e^{-E_j/kT_t}}{\sum e^{-E_j/kT_t}} e^{-(D-E_j)/kT_t} \quad (B63)$$

and comparing it with the expression for k_{deg} determined experimentally, namely,

$$[k_{deg}]_{\text{exp}} = a T_t^n e^{-\theta_D/T_t} \quad (\text{c.c./mole sec}) \quad (B64)$$

where a and n are constants determined from experiment, U as a function of T_t is found as a solution of the equation obtained by equating k_{deg} from Eqs. (B63) and (B64), that is

$$\begin{aligned} a T_t^n e^{-\theta_D/T_t} &= c Z_0 e^{-D/kU} e^{-D/kT_t} \frac{Q(-U)}{Q(T_t)} \\ &= c Z_0 e^{-\theta_D/U} e^{-\theta_D/T_t} \frac{Q(-U)}{Q(T_t)} \end{aligned}$$

$$\text{or} \quad \frac{e^{\theta_D/U}}{Q(-U)} = \frac{c Z_0}{a T_t^n Q(T_t)} \quad (B65)$$

As noted in Section 3.3.1, $C=1$ for $U = \infty$.

In the simple harmonic oscillator approximation,

$$Q(T_t) = \sum e^{-E_j/kT_t} = (1 - e^{-\theta_v/T_t})^{-1} \quad (B66)$$

and

$$Q(U) = \sum e^{E_j/kU} = \sum_j e^{j\theta_v/U} \quad (B67)$$

where θ_v is the characteristic temperature for vibration. Thus U is obtained as a function of T_t for the simple harmonic oscillator approximation as

$$\frac{e^{\frac{\theta_v}{U}}}{\sum_j e^{j\theta_v/U}} = c Z_o \frac{(1 - e^{-\theta_v/T_t})}{a T_t^n} \quad (B68)$$

For example for the case of oxygen molecule-molecule collisions

$$\begin{aligned} n &= -2.5 \\ a &= 0.073 \times 7.43 \times 10^{-8} \theta_v^3 \end{aligned} \quad (B69)$$

in the temperature range $T_t = 3700^\circ\text{K}$ to 5000°K from Ref. 32 where the dimensions of $(a T_t^n)$ is cc/mole sec.

Eq. (B68) is a transcendental equation and the evaluation of U as a function of T_t is quite complicated. The collision number Z_o in Eq. (B68) is given explicitly as (see Ref. 29) for like molecule-molecule collisions.

$$Z_{022} = \frac{\alpha_2^2}{\sqrt{2}} \sqrt{\frac{8\pi k T_t}{m_2}} = A_{22} T_t^{1/2} \quad (B70)$$

and for atom-molecule collisions

$$Z_{012} = \frac{1}{4} (\alpha_1 + \alpha_2)^2 \sqrt{\frac{8\pi k T_t}{\mu_{12}}} = A_{12} T_t^{1/2} \quad (B71)$$

where α_1, α_2 are collision radii for molecule-molecule and atom-molecule collisions, and μ_{12} is the reduced mass of the atom and molecule and is given by

$$\mu_{12} = \frac{m_1 m_2}{m_1 + m_2} \quad (B72)$$

where m_1, m_2 are the masses of atom and molecule. For oxygen $\alpha_1 = 2.96 \times 10^{-8} \text{ cm}$ and $\alpha_2 = 3.54 \times 10^{-8} \text{ cm}$ (see Ref. 38).

Approximation for U

Consider the molecule-molecule collisions and substitute for Z_o from

Eq. (B70) into Eq. (B68) and for $\frac{\theta_v}{T_t} < 1$, expand the numerator on RHS in Eq. (B68), then

$$\begin{aligned} \frac{e^{\theta_v/U}}{\sum e^{j\theta_v/U}} &= \frac{A_{22} T_t^{1/2}}{a T_t^n} \left[\frac{\theta_v}{T_t} - \frac{1}{2} \left(\frac{\theta_v}{T_t} \right)^2 + \dots \right] \\ &= \frac{A_{22} \theta_v}{a} T_t^{-n+1/2} \left[1 - \frac{1}{2} \frac{\theta_v}{T_t} + \dots \right] \\ &\approx B T_t^{(-n+1/2)} \end{aligned} \quad (B73)$$

where

$$B = \frac{A_{22} \theta_v}{a} = \text{constant} \quad (B74)$$

Relative Efficiencies of Atoms and Molecules

In section 3.1.2, an expression for the number of dissociations per sec per cc Z_d is given in Eq. (64) as

$$Z_d = P \cdot Z \cdot \frac{(E^*/RT)^\delta}{\delta!} e^{-E^*/RT} \quad (B75)$$

where Z , the total number of collisions is

$$Z = Z_0 n_A n_B \quad (B76)$$

where Z_0 is the collision number, i.e. the total number of collisions per sec per cc per unit concentrations of reactants and n_A , n_B are number densities of reactants per cc. Z_0 for molecule-molecule and atom-molecule collisions are given in Eqs. (B70) and (B71).

From Eqs. (B75), (B76), $Z_{d0} = \frac{Z_d}{n_A n_B} = k_d$ can be written as

$$k_d = \frac{Z_d}{n_A n_B} = Z_{d0} = P \cdot Z_0 \cdot \frac{(E^*/RT)^\delta}{\delta!} e^{-E^*/RT} \quad (B77)$$

As pointed out in Section 3.1.2, $\delta = 2$ and 1 for molecule-molecule and atom-molecule collisions respectively because of the differing number of vibrational modes entering into the collisions and thus if k_{da} is the rate coefficient and P_a the probability for atom-molecule collisions, then

$$\lambda = \frac{k_{da}}{k_d} = \frac{P_a}{P} \cdot \frac{Z_{012}}{Z_{022}} \frac{1}{2!} \left(\frac{E^*}{RT} \right)^{-1} \quad (B78)$$

for oxygen

$$\frac{Z_{012}}{Z_{022}} = \frac{\frac{1}{4} (a_1 + a_2)^2 \sqrt{\frac{8\pi RT_t}{m_{12}}}}{\frac{1}{\sqrt{2}} a_2^2 \sqrt{\frac{8\pi RT_t}{m_2}}} \quad (B79)$$

from Eqs. (B70), (B71) where $\alpha = 2.96 \times 10^{-8}$, $\alpha_2 = 3.54 \times 10^{-8}$ and μ_{12} is given in Eq. (B72) and $m_2 = 2m = 2m_1$, where m is the mass of an oxygen atom. Thus

$$\begin{aligned} \frac{Z_{012}}{Z_{022}} &= \frac{\sqrt{2}}{4} \left(1 + \frac{\alpha_1}{\alpha_2}\right)^2 \sqrt{\frac{2m(m+2m)}{m \cdot 2m}} \\ &= \frac{\sqrt{1.5}}{2} \left(1 + \frac{2.96}{3.54}\right)^2 \\ &= 1.1 \end{aligned} \quad (\text{B80})$$

Also from Byron's experimental results (Ref. 33)

$$k_{da} = Z_{012} 5.216 k_3 \left(\frac{\theta_D}{T_t}\right) e^{-\theta_D/T_t} \quad (\text{B81})$$

$$k_d = Z_{022} \frac{2.104 k_4}{n!} \left(\frac{\theta_D}{T_t}\right)^n e^{-\theta_D/T_t} \quad (\text{B82})$$

where $n=2$ and $k_3=1.7$, $k_4=0.24$. Thus λ is given by

$$\begin{aligned} \lambda = \frac{k_{da}}{k_d} &= \frac{Z_{012}}{Z_{022}} \cdot \frac{5.216 \times 1.7}{2.104 \times 0.24/2} \left(\frac{\theta_D}{T_t}\right)^{-1} \\ &\approx 35 \frac{T_t}{\theta_D} \end{aligned} \quad (\text{B83})$$

Equilibrium Constant K_C

The equilibrium constant K_C is from Eq. (B25),

$$K_C = \frac{k_{deg}}{k_n} \quad (\text{B25})$$

where k_{deg} , k_n are the dissociational and recombination rate constants for vibrational and translational equilibrium. Also for thermal and chemical equilibrium, from Eq. (60)

$$K_C = \left(\frac{[A]^2}{[A_2]} \right)_{eq} \quad (60)$$

where $[A]$, $[A_2]$ in terms of α are:

$$[A] = \frac{p\alpha}{m_a} \quad (\text{B27})$$

$$[A_2] = \frac{p(1-\alpha)}{2m_a} \quad (\text{B28})$$

Thus

$$K_C = \frac{\rho^2 \alpha_e^2}{m_a^2} \cdot \frac{\rho(1-\alpha_e)}{2m_a} \quad (B84)$$

$$= \frac{2\rho}{m_a} \cdot \frac{\alpha_e^2}{1-\alpha_e}$$

Also for vibrational and dissociational equilibrium, from Eq. (A34),

$$\frac{\alpha_e^2}{1-\alpha_e} = \frac{2\rho_D}{\rho} \left(\frac{T}{\theta_v}\right)^{\frac{1}{2}} (1-e^{-\theta_v/T}) e^{-\theta_v/T} \quad (A34)$$

Hence

$$K_C = \frac{4\rho_D}{m_a} \cdot \left(\frac{T}{\theta_v}\right)^{\frac{1}{2}} (1-e^{-\theta_v/T}) e^{-\theta_v/T} \quad (B85)$$

where ρ_D is given in Eq. (A16).

Relation Between k_{rj} , $k_{dj,eq}$ and K_C

A relation between the recombinational and dissociational rate constants for vibrational level j under vibrational equilibrium can be obtained as follows:-

For vibrational and dissociational equilibrium, Eqs. (B11), (B12), (B13) give.

$$\sum Z_{rj} = \sum Z_{dj} \quad (B86)$$

$$\text{or } [A]_{eq}^2 [A_2]_{eq} \sum k_{rj} = k_n [A]_{eq}^2 [A_2]_{eq} = [A_2]_{eq} \sum k_{dj,eq} [A]_{eq} = [A_2]_{eq}^2 k_{d,eq}$$

$$[A]_{eq}^2 \sum k_{rj} = \sum k_{dj,eq} [A]_{eq} \quad (B87)$$

$$[A]_{eq}^2 \left\{ \sum k_{rj} - k_{dj,eq} \frac{[A]_{eq}}{[A]_{eq}^2} \right\} = 0 \quad (B88)$$

By the principle of detailed balancing one has

$$k_{rj} = k_{dj,eq} \frac{[A]_{eq}}{[A_2]_{eq}} \cdot \frac{[A_2]_{eq}}{[A]_{eq}^2} \quad (B89)$$

$$= \frac{1}{K_C} k_{dj,eq} \frac{[A]_{eq}}{[A_2]_{eq}}$$

From Eq. (B13)

$$k_{dj} [A_j] [A_2] = Z_{dj} = C Z_0 \rho_j N_j N_2 m (D - E_j)$$

$$\begin{aligned}
 k_{dj} &= c Z_0 P_j M(D-E_j) \\
 &= c Z_0 e^{-(D-E_j)/kT_t} e^{-(D-E_j)/kT_t} \\
 k_{dj} \cdot \frac{[A]_{eq}}{[A]_{eq}} &= c Z_0 e^{-(D-E_j)/kT_t} \frac{e^{-E_j/kT_t}}{\sum e^{-E_j/kT_t}} e^{-(D-E_j)/kT_t} \\
 &= c Z_0 e^{-D/kT_t} e^{-E_j/kT_t} / Q(T_t)
 \end{aligned} \tag{B90}$$

Dissociation Rate with Internal Energy Taken into Account

In section 3.3.1, Z_{dj} the number of dissociations from level j is assumed to be of the form

$$Z_{dj} = c Z_0 P_j N_j N M(D-E_j)$$

where $M(D-E_j)$ is the fractional number of collisions with a relative kinetic energy greater than $D-E_j$ along the line of centers. The expression for this is taken as

$$M(D-E_j) = \exp \left[-(D-E_j)/kT_t \right]$$

In section 3.1.2, the overall rate for vibration in equilibrium with translation or Z_{dj} summed over all levels was shown to consist of an additional factor $(E^*/kT)^s/s!$ (Eq. (64)) if one wishes to take into account the internal energies of the colliding partners as well.

Suppose that vibrational energy of all molecules taking part in a collision can contribute to the energy of dissociation.

Consider "nonequilibrium" situation, i.e. $T_t = T_v$.

(a) Dissociation rate, molecule-atom collisions:

This is, of course, the same as already evaluated:

$$\text{Rate} = \sum_j Z_{dj}^a = \sum_j c Z_0^a P_j [A] [A_j] m(D-E_j)$$

The internal energy of the molecule is taken into account in this formulation.

(b) Dissociation rate, molecule-molecule collisions:

Consider two colliding molecules, one with vibrational energy E_j , the other with energy E_l .

$$\text{Total energy} = E_j + E_l$$

Energy required for dissociation = $D - (E_j + E_e)$

Probability that translational energy of collision along line of centres exceeds this amount, is $e^{-(D-E_j-E_e)/kT_t}$

$$\text{Rate} = \frac{1}{2} \sum_j \sum_l P_{jl} \cdot c Z_0 [A_j] [A_l] e^{-(D-E_j-E_e)/kT_t}$$

α , the symmetry number, = 2 for collisions between like molecules (e.g. $O_2 - O_2$ collisions), so that collisions are counted only once in the summation.

$\alpha = 1$ for collisions between unlike molecules.

Assume collisions between like molecules, i.e. $\alpha = 2$.

Consider the form of P_{jl} .

By analogy with P_j , P_{jl} could be put in the form:

$$P_{jl} = e^{-(D-E_j-E_e)/kU}$$

$$\therefore k_d^m = \frac{\text{Rate}}{[A_2]^2} = \frac{c Z_0}{2} \sum_j \sum_l e^{-(D-E_j-E_e)/kU}$$

$$\begin{aligned} & \times \frac{[A_j][A_l]}{[A_2][A_2]} e^{-(D-E_j-E_e)/kT_t} \\ &= \frac{c Z_0}{2} e^{-D/kU} e^{-D/kT_t} \sum_j \left(\sum_k e^{E_k/kU} \frac{e^{-E_k/kT_t} e^{E_k/kT_t}}{Q(T_t)} \right) \\ & \quad \times e^{E_j/kU} \frac{e^{-E_j/kU} e^{E_j/kT_t}}{Q(T_t)} \\ &= \frac{c Z_0}{2} e^{-D/kU} \cdot e^{-D/kT_t} \sum_j \frac{Q(T_t)}{[Q(T_t)]^2} e^{E_j/kU} e^{-E_j/kT_t} e^{E_j/kT_t} \\ &= \frac{c Z_0}{2} e^{-D/kU} \cdot e^{-D/kT_t} \frac{Q^2(T_f)}{Q^2(T_t)} \end{aligned}$$

where $\frac{1}{T_f} = \frac{1}{T_t} - \frac{1}{U}$

when $T_t = T_t$, $k_d^m = k_{deg}^m$, $T_f = -U$

$$\therefore V^m = \frac{k_d^m}{k_{deg}^m} = \frac{Q^2(T_f)}{Q^2(T_t)} \cdot \frac{Q^2(T_t)}{Q^2(-U)}$$

But for molecule-atom collisions,

$$\frac{k_d^a}{k_{deg}^a} = V^a = \frac{Q(T_f)}{Q(T_v)} \cdot \frac{Q(T_e)}{Q(-U)}$$

$$\therefore V^m = (V^a)^2$$

APPENDIX C

Equations for Limiting Flows

It has been pointed out in Section 4.2.2 that the limiting cases of equilibrium and frozen flows can be determined as the solution of a system of algebraic equations. These equations will be derived in this appendix for vibrational and dissociational equilibrium, called here equilibrium flow, and for vibrational equilibrium and frozen dissociation, called here partially frozen flow.

Equilibrium Flow

When vibration and dissociation are in equilibrium $T_t = T_v$ and $\alpha_e = \alpha_e(p, T_t)$. The dependence of α_e on local p , T_t is shown in Appendix A to be

$$X(\alpha, p, T_t) = \frac{\alpha_e^2}{1-\alpha_e} - \frac{2p_D}{p} \left(\frac{T_t}{\theta_v} \right)^{\frac{1}{2}} (1 - e^{-\theta_v/T_t}) e^{-\theta_v/T_t} = 0 \quad (C1)$$

In addition, one has the mass, energy and state equations

$$\rho q A = \dot{m}_e = \text{constant} \quad (C2)$$

$$h + \frac{q^2}{2} = h_0 = \text{constant} \quad (C3)$$

$$p = \rho R T_t (1 + \alpha_e) \quad (C4)$$

and the momentum equation in differential form

$$q dq + \frac{dp}{\rho} = 0 \quad (C5)$$

Here p , ρ , q , T_t , α , A , h are the pressure, density, speed, temperature, atom mass fraction, nozzle area and enthalpy respectively. It has been shown in Appendix A that the enthalpy h can be expressed in terms of α , T_t , ϵ_v . In equilibrium $\epsilon_v = \epsilon_v(T_t)$ and hence h is a function of α and T_t , alone. Thus once the reservoir conditions are known, one can compute h_0 , thus completing Eq. (C3). It has been shown in Section 4.2.2 that the entropy remains constant and this condition can be used to replace the differential momentum equation (C5).

This is achieved as follows:-

Write equations (C1), (C3), (C4) in differential form:

$$X_\alpha \frac{d\alpha_e}{dx} + X_p \frac{dp}{dx} + X_{T_t} \frac{dT_t}{dx} = 0 \quad (C6)$$

$$h_\alpha \frac{d\alpha_e}{dx} + h_{T_t} \frac{dT_t}{dx} + q \frac{dq}{dx} = 0 \quad (C7)$$

$$\frac{1}{p} \frac{dp}{dx} + \frac{1}{f} \frac{df}{dx} + \frac{1}{T_t} \frac{dT_t}{dx} + \frac{1}{1+\alpha_e} \frac{d\alpha_e}{dx} = 0 \quad (C8)$$

On combining equations (C5) and (C8) one has

$$f \frac{df}{dx} + \frac{R(1+\alpha_e)T_t}{f} \frac{df}{dx} + R(1+\alpha_e) \frac{dT_t}{dx} + RT_t \frac{d\alpha_e}{dx} = 0 \quad (C9)$$

Eliminating $\frac{df}{dx}$, $\frac{dp}{dx}$ from equations (C6), (C7) and (C9), one obtains

$$\frac{d\alpha}{dx} \left[-\frac{h_\alpha}{R} + T_t - \frac{(1+\alpha)T_t}{f x_p} x_\alpha \right] + \frac{dT_t}{dx} \left[-\frac{h_{T_t}}{R} + (1+\alpha) - \frac{(1+\alpha)T_t}{f x_p} x_{T_t} \right] = 0 \quad (C10)$$

From the expressions for h and x in terms of α , f , T_t one can evaluate the partial derivatives occurring in Eq. (C10) as

$$\frac{h_\alpha}{R} = \frac{3}{2} T_t - \frac{\theta_v}{e^{\theta_v/T_t} - 1} + \theta_D \quad (C11)$$

$$\frac{h_{T_t}}{R} = \frac{7+3\alpha}{2} + (1-\alpha) \left(\frac{\theta_v/T_t}{e^{\theta_v/T_t} - 1} \right)^2 e^{\theta_v/T_t} \quad (C12)$$

$$x_\alpha = \frac{\alpha(2-\alpha)}{(1-\alpha)^2} \quad (C13)$$

$$f x_p = \frac{\alpha^2}{1-\alpha} \quad (C14)$$

$$x_{T_t} = -\frac{\alpha^2}{1-\alpha} \left[\frac{1}{2T_t} + \frac{\theta_D}{T_t^2} - \frac{\theta_v/T_t^2 e^{-\theta_v/T_t}}{1 - e^{-\theta_v/T_t}} \right] \quad (C15)$$

Substitution of expressions (C11)-(C15) in Eq. (C10) gives

$$\frac{d\alpha}{dx} \left[-\theta_D + \frac{\theta_v}{e^{\theta_v/T_t} - 1} - \frac{3T_t}{2} - 2T_t \left(\frac{1}{\alpha} + \frac{1}{1-\alpha} \right) \right] + \frac{dT_t}{dx} \left\{ -2 + \frac{(1+\alpha)\theta_D}{T_t} - (1-\alpha) \left(\frac{\theta_v/T_t}{e^{\theta_v/T_t} - 1} \right)^2 e^{\theta_v/T_t} - (1+\alpha) \frac{\theta_v/T_t}{e^{\theta_v/T_t} - 1} \right\} = 0 \quad (C16)$$

Dividing throughout by T_t , this equation can be put in a perfect differential form, namely

$$-d \left[\frac{3\alpha}{2} + 2 \log \alpha - 2 \log (1-\alpha) + 2 \log T_t + \frac{(1+\alpha)\theta_D}{T_t} \right] - d \left[(1-\alpha) \frac{\theta_v/T_t}{e^{\theta_v/T_t} - 1} \right] + 2 d \left[\log (1 - e^{-\theta_v/T_t}) \right] = 0 \quad (C17)$$

Integrating, one obtains

$$\frac{3\alpha}{2} + 2 \log \frac{\alpha T_t}{(1-\alpha)(1 - e^{-\theta_v/T_t})} + (1+\alpha) \frac{\theta_D}{T_t} + (1-\alpha) \frac{\theta_v/T_t}{e^{\theta_v/T_t} - 1} = \text{Constant} \quad (C18)$$

The integration constant may be evaluated at the reservoir condition α_0 , T_{t0} . By comparing Eq. (C18) with the expression given for entropy in Eq. (A15) of Appendix A, it will be seen that Eq. (C18) simply expresses

the fact that entropy is constant in an equilibrium flow.

Thus for the evaluation of p , ρ , T_t , α , g in an equilibrium flow, one can use Eqs. (C1) to (C4) and Eq. (C18). To complete the problem, one still requires the knowledge of the equilibrium mass flow \dot{m}_e . This can be determined as follows:-

The mass conservation equation in differential form is

$$\frac{1}{\rho} \frac{d\rho}{dx} + \frac{1}{g} \frac{dg}{dx} + \frac{1}{A} \frac{dA}{dx} = 0 \quad (C19)$$

For the derivatives in the system of equations (C6), (C7), (C9), (C19) to have a nontrivial solution, when $\frac{dA}{dx} = 0$, the determinant of the coefficients of these derivatives in these equations should be zero, i. e.

$$\begin{vmatrix} x_p & x_\alpha & x_{T_t} & 0 \\ 0 & h_\alpha & h_{T_t} & g \\ 1/p & 0 & 0 & 1/g \\ \frac{R(\alpha)T_t}{\rho} & RT_t & R(\alpha) & g \end{vmatrix} = 0 \quad (C20)$$

or

$$g^2[(\alpha)RX_\alpha - RT_tX_{T_t} + h_\alpha x_{T_t} - x_\alpha h_{T_t}] + R(\alpha)p[h_\alpha - T_t h_{T_t}] + R(\alpha)T_t(h_\alpha - x_{T_t} h_\alpha) = 0 \quad (C21)$$

Eqs. (C1), (C3), (C4), (C18), (C21) can be solved for the critical values of p , ρ , T_t , g , α at the geometrical throat from which the equilibrium mass flow \dot{m}_e can be calculated. Once the mass flow is determined Eqs. (C1) to (C4) and Eq. (C18) are complete and can be used for finding the equilibrium flow properties for a prescribed area variation in a nozzle.

Partially frozen flow

In a partially frozen flow vibration is in equilibrium with translation giving $T_t = T_v$ and dissociation is frozen, that is $\frac{d\alpha}{dx} = 0$. Thus one has to

determine only p , ρ , T_t , g . In addition to the mass, energy and state equations (C2), (C3), (C4) one can derive another equation giving a relation between ρ and T_t by eliminating $\frac{dg}{dx}$ from (C7) and (C9).

For the partially frozen case, Eqs. (C7), (C9) simplify to

$$h_{T_t} \frac{dT_t}{dx} + g \frac{dg}{dx} = 0 \quad (C22)$$

$$g \frac{dg}{dx} + \frac{R(\alpha)T_t}{\rho} \frac{d\rho}{dx} + R(\alpha) \frac{dT_t}{dx} = 0 \quad (C23)$$

Elimination of $\frac{dq}{dx}$ from eqs. (B22), (B23) gives

$$\left[\frac{h_{T_t}}{R} - (1+\alpha) \right] \frac{R dT_t}{dx} - \frac{R(1+\alpha)T_t}{\rho} \frac{d\rho}{dx} = 0 \quad (C24)$$

Substituting for h_{T_t} from Eq. (C12) and integrating, one gets

$$\log \rho - \frac{5+\alpha}{2(1+\alpha)} \log T_t - \frac{(1+\alpha)}{1+\alpha} \left[\frac{\theta_v/T_t}{e^{\theta_v/T_t} - 1} - \log(1 - e^{-\theta_v/T_t}) \right] = \text{Constant} \quad (C25)$$

Here the integration constant can be evaluated at the reservoir conditions. Eq. (C25) simply expresses the fact that entropy is constant in a partially frozen flow. Eqs. (C2)-(C4) and (C25) can be used to evaluate frozen flow properties. However the mass conservation equation (C2) contains the unknown the frozen mass flow \dot{m}_f . This can again be evaluated as in the equilibrium case by starting with Eqs. (C19), (C22) and (C23) and requiring that, for $\frac{dA}{dx} = 0$, these equations have a nontrivial solution for their de-

derivatives, that is that the determinant of the coefficients of the derivatives be zero, giving

$$\begin{vmatrix} 0 & \frac{1}{\rho} & \frac{1}{q} \\ R_{T_t} & 0 & q \\ R(1+\alpha) & R \frac{(1+\alpha)T_t}{\rho} & q \end{vmatrix} \quad (C26)$$

or

$$q^2 [R_{T_t} - R(1+\alpha)] - R(1+\alpha)T_t R_{T_t} = 0 \quad (C27)$$

Eqs. (C3), (C4), (C25), (C27) can be solved for the critical values of ρ , ρ , T_t , q at the nozzle throat from which the frozen mass flow \dot{m}_f can be evaluated.

Fully Frozen Flow

For frozen vibration and dissociation, the situation is exactly the same as in the partially frozen case except that in the expression for R_{T_t} given in Eq. (C12), the second term on the right hand side drops out which is nothing but the vibrational contribution. Also the third term on the left hand side in Eq. (C25) does not appear because of the change in h_{T_t} .

APPENDIX D

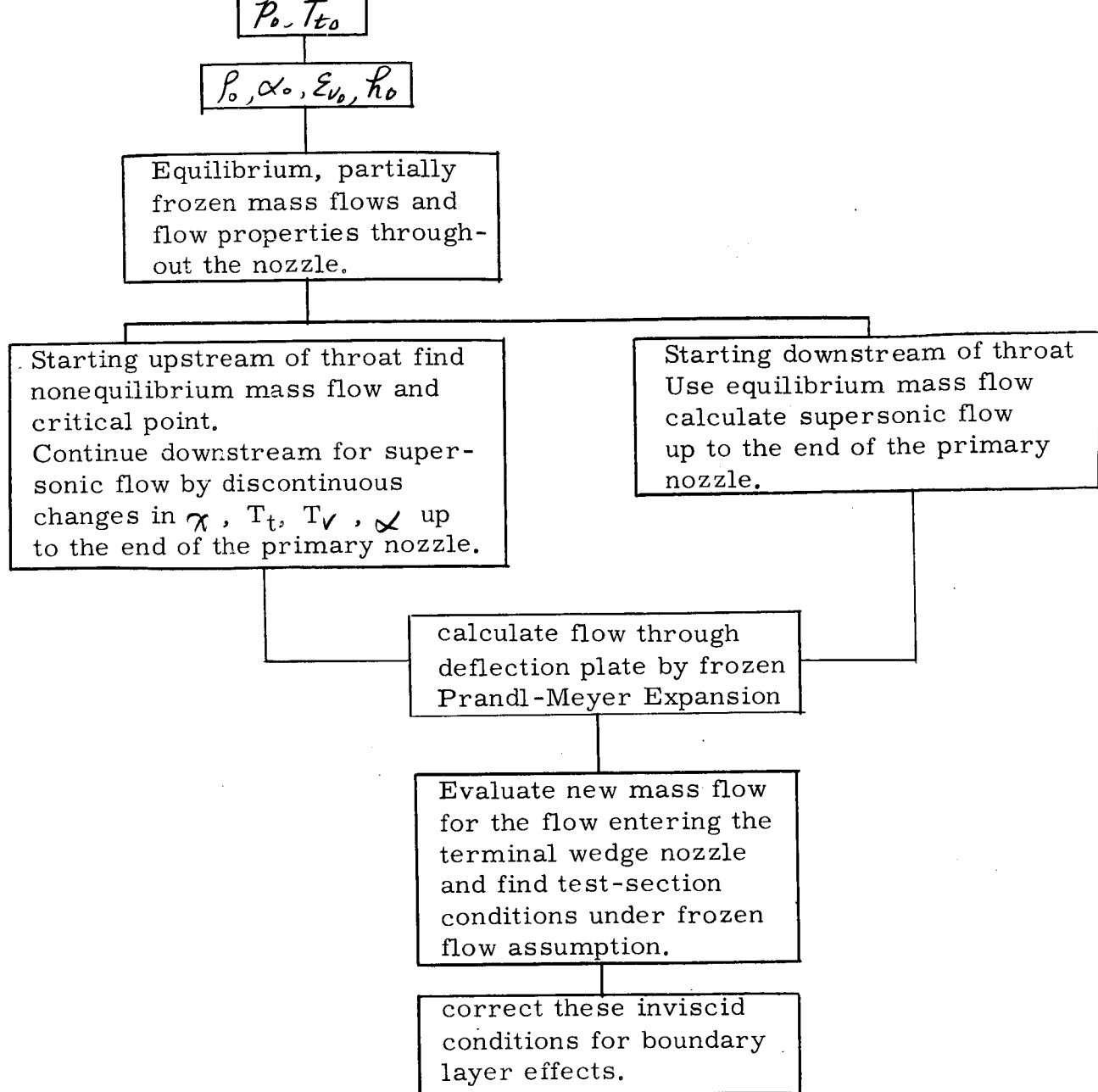
Computer Programme

The nonequilibrium flow equations derived in Appendix B were solved numerically on an IBM 7090 digital computer at the Institute of Computer Science of the University of Toronto. The computer programme was written in Fortran II language. Since the calculations involved the integration of coupled ordinary differential equations for T_t , α and \mathcal{E}_v or T_v , a fourth order Runge-Kutta method of integration was used. It was shown by Emmanuel and Vincenti (Ref. 14) that for such a problem as this, the fourth order Runge-Kutta method is quite adequate. As discussed in Section 5.3 the nonequilibrium calculations were started from initial equilibrium conditions and contained a mechanism for progressive increase of integration step size as suggested in Ref. 14.

The first step in the main programme was the evaluation of α , ρ for the given reservoir conditions ρ_0 , T_{t0} by the equilibrium relation between α , ρ , T and the state equation. Then the equilibrium and the partially frozen mass flows were evaluated, and the equilibrium and partially frozen flow properties throughout the nozzle were calculated by use of the equations derived in Appendix C. For nonequilibrium flow calculations starting upstream of the geometrical throat, a nonequilibrium mass flow between the equilibrium and partially frozen mass flows was chosen and the calculations were repeated in an iteration procedure until the true nonequilibrium mass flow and the critical point were obtained. The calculations were then continued downstream by means of the jump conditions applied to χ , T_t , T_v and α as discussed in Section 5.3 to obtain supersonic flow, (that is frozen Mach number $M_f > 1$) in the divergent portion of the nozzle. For the UTIAS Hypersonic shock tunnel calculations, the further expansion of the flow past the deflection plate and a terminal wedge nozzle were calculated under the assumption of fully frozen flow. In the terminal wedge nozzle only the test section conditions were evaluated. The frozen flow assumption in these later expansions was made since at the end of the primary nozzle $\frac{d\alpha}{dx}$ and $\frac{d\mathcal{E}_v}{dx}$ were of the order of 10^{-3} .

To these inviscid results in the test-section, boundary layer corrections were applied using the formula for boundary layer displacement thickness δ^* given by Burke and Bird (Ref. 39) for turbulent flows.

These various steps are shown in the flow diagram given below.



For the evaluation of the various steps in the main programme several subprogrammes were written. They were:

SUMEJ: For the evaluation of $Q(T_t)$, $Q(T_v)$, $Q(T_f)$, $Q(-U)$ and $\mathcal{E}(T_f)$, $\mathcal{E}(T_t)$, $\mathcal{E}(T_v)$, $\mathcal{E}(-U)$. As indicated in Section 5.2, the vibrational energy and the partition functions were evaluated through a summation of exponentials to take into account slight anharmonicities.

FUN 3: For the evaluation of partially frozen flow properties throughout the nozzle as a solution of Eqs. (C3), (C4), (C25), (C27) -- uses subprogramme FUNRO, FUNHT.

FUN 4: For the evaluation of partially frozen flow properties throughout

- the nozzle as a solution of Eqs. (C2), (C3), (C4) and (C25) -- Uses subprogramme FUNRO.
- FUN 5: For the evaluation of equilibrium mass flow as a solution of Eqs (C1), (C3), (C4), (C18) and (C21) -- Uses subprogrammes FUN 51, FUN 52, FUN 53, FUN RO2 and library tape subroutine JCPM.
- FUN 51: Equation (C21) -- Uses subprogramme FUNHT.
- FUN HT: h_{T_t} - Eq. (C12)
- FUN 52: Equation (C18)
- FUN 53: LHS Of Eq. (C18)
- FUN 6: For the evaluation of equilibrium flow properties throughout the nozzle as a solution of Eqs. (C1) to (C4) and (C18) -- Uses subprogrammes FUN 52, FUN 53, RUNRO2 and Library Tape subroutine JCPM.
- FUNRO: Eq. (C25) gives ρ as a function of α and T_t for partially frozen flows.
- FUNRO2: Eq. (C1) -- gives ρ as a function of α , T_t for equilibrium flow.
- SEARCH: For the solution of two unknowns T_t , α from algebraic - transcendental equations (C1), (C3), (C4), (C18), and (C21) or (C1) to (C4) and (C18) -- Used for evaluation of equilibrium mass flow, equilibrium flow properties in the nozzle and initial conditions for starting nonequilibrium flow calculations.
- EQUIL1: For calculating partially frozen or equilibrium flow properties throughout the nozzle.
- INTEGR: For integration of the nonequilibrium flow equations, controls integration step size, output printing interval, total number of steps and total time used -- Uses subprogrammes DERIV, TEST, END and Library Tape subroutines DEQ, DEQST.
- DERIV7: For the evaluation of the derivatives $\frac{d\alpha}{dx}$, $\frac{d\varepsilon_v}{dx}$, $\frac{dT_t}{dx}$ used by DEQ and DEQST in the integration by fourth order Runge-Kutta method.
- TEST 7: For the evaluation of the critical nonequilibrium mass flow for nonequilibrium calculations starting upstream of the throat and for the prescription of jump conditions in x , T_t , T_v , α for calculations downstream of the critical point -- used only in

the calculations starting upstream of the throat.

END 7: a dummy subroutine.

TEST 7: (Dummy) a dummy subroutine for calculations starting downstream of the throat.

FUNPM: for calculation of flow past the deflection plate through a frozen Prandtl-Meyer expansion.

FUNT: for calculation of flow through the terminal wedge nozzle under frozen flow assumption.

FUNH: for the evaluation of enthalpy.

FUNA: for the nozzle area ratio variations.

SOLN: for calculating the boundary layer effect on the inviscid conditions by iteration.

UROPMS: for evaluation of the various flow properties under frozen and equilibrium assumptions.

DERIV4: for the calculation of partially frozen flows through integration of $\frac{dT_t}{dx} = \frac{q^2 \frac{1}{A} \frac{dA}{dx}}{(1-M_f^2) h_{T_t}}$ -- uses subprogrammes FUNDT, FUNA, FUNH.

TEST 4) : dummy subroutines for frozen calculations by integration.
END 4)

DERIV6: for the calculation of equilibrium flows through integration of $\frac{dT_t}{dx} = \frac{q^2 \frac{1}{A} \frac{dA}{dx}}{(1-M_e^2) h_{T_t}}$ -- uses subprogrammes FUNDT, FUNA, FUNH.

TEST 6) : dummy subroutines for equilibrium calculations by integration.
END 6)

FUNDT: calculates $\frac{q^2}{(1-M^2) h_{T_t}}$ for partially frozen and equilibrium flows with the corresponding h_{T_t} and M^2 , i. e. M_f^2 and M_e^2 respectively.

The various Fortran names occurring in each of these subprogramme and their expression in non-dimensional form are given in the following pages.

Non-Dimensionalisation

For the calculations on the computer, all the flow variables and rate constants

were non-dimensionalised as follows:-

$p_0, T_{t0}, \rho_0, \alpha_0$ pressure, translational temperature, density,
atomic mass fraction in the reservoir (dimensional)
 $k_{r0}, \tau_{v0}, K_{c0}$ recombination rate constant, vibrational relaxation
time, equilibrium constant at reservoir conditions.
(dimensional)

A^* throat area.

All quantities with dimensions of temperature are non-dimensionalised by T_{t0} namely, (primed quantities are dimensional).

$$T_t = \frac{T_t'}{T_{t0}}, T_v = \frac{T_v'}{T_{t0}}, U = \frac{U'}{T_{t0}}, T_f = \frac{T_f'}{T_{t0}}, \theta_2 = \frac{\theta_2'}{T_{t0}}, \theta_1 = \frac{\theta_1'}{T_{t0}}, \theta_n = \frac{\theta_n'}{T_{t0}} \quad (D1)$$

pressure $p = \frac{p'}{p_0} = p T_t (1+\alpha)/(1+\alpha_0) \quad (D2)$

density $\rho = \frac{\rho'}{\rho_0} \quad (D3)$

enthalpy $h = \frac{h'}{R T_{t0}} = \frac{7+3\alpha}{2} T_t + (1-\alpha) \theta_1 + \alpha \theta_2 \quad (D4)$

speeds $g = \frac{g'}{\sqrt{R T_{t0}}}, a_f = \frac{a_f'}{\sqrt{R T_{t0}}} = \sqrt{\frac{7+3\alpha}{5+\alpha} (1+\alpha) T_t} \quad (D5)$

area $A = A / A^* \quad (D6)$

Rates are non-dimensionalised by their reservoir values, namely

$$SMKR = k_n = \frac{k_n'}{k_{n0}} = T_t^{d_2} \exp \frac{d_1}{T_t} \left(\frac{1}{T_t} - 1 \right) \quad (D7)$$

$$\tau_v = \frac{\tau_v'}{\tau_{v0}} = \frac{1}{p} \exp \left[b_1 T_t^{b_2} (T_t^{b_2} - 1) \right] \quad (D8)$$

$$K_c = \frac{K_c'}{K_{c0}} = \frac{(T_t)^{\frac{1}{2}} (1 - e^{-\theta_1/T_t}) e^{-\theta_2/T_t}}{(1 - e^{-\alpha}) e^{-\theta_2}} \quad (D9)$$

where

$$k_{n0} = T_{t0}^{d_2} \exp(d_0 + d_1/T_{t0}) = SMKROD \quad (D10)$$

$$\tau_{v0} = \frac{1}{p_0} b_0 \exp(b_1 T_{t0}^{b_2}) = TAUOD \quad (D11)$$

$$K_{c0} = \frac{4\rho_0}{m_a} \left(\frac{T_{t0}}{\theta_1'} \right)^{\frac{1}{2}} (1 - e^{-\theta_1'/T_{t0}}) e^{-\theta_2'/T_{t0}} = \frac{4\rho_0}{m_a} (\theta_1')^{\frac{1}{2}} (1 - e^{-\alpha}) e^{-\theta_2} \quad (D12)$$

To vary τ_v from its normal shock value, a parameter $D\tau$ is introduced such that

$$TAUOV = D\tau * \tau_{v0} \quad (D11^i)$$

With this non-dimensionalisation, the equations transform as follows:

Equilibrium flow:-

The equilibrium relation between α , ρ , T_t becomes

$$\begin{aligned} \frac{\alpha^2}{1-\alpha} &= \frac{2\rho_D}{\rho'} \left(\frac{T_t'}{\theta_v'} \right)^{1/2} (1 - e^{-\theta_v'/T_t'}) e^{-\theta_v'/T_t'} \\ &= \frac{2\rho_D}{\rho_0 \rho} \left(\frac{T_t}{\theta_v} \right)^{1/2} (1 - e^{-\theta_v/T_t}) e^{-\theta_v/T_t} \end{aligned} \quad (D13)$$

from which ρ may be written as a function of α_e , T_t in equilibrium as

$$\rho = \frac{2\rho_D}{\rho_0} \left(\frac{T_t}{\theta_v} \right)^{1/2} (1 - e^{-\theta_v/T_t}) e^{-\theta_v/T_t} \frac{(1-\alpha_e)}{\alpha_e^2} \quad (D14)$$

which for the reservoir conditions $T_t' = T_{t0}$, $\alpha_e = \alpha_0$, $\rho' = \rho_0$ or $T_t = 1$, $\rho = 1$ becomes $1 = \frac{2\rho_D}{\rho_0} \left(\frac{1}{\theta_v} \right)^{1/2} (1 - e^{-\theta_v}) e^{-\theta_v} \frac{(1-\alpha_0)}{\alpha_0^2}$ (D15)

Dividing Eq. (D14) by Eq. (D15), we obtain

$$\rho = (T_t)^{1/2} (1 - e^{-\theta_v/T_t}) e^{-\theta_v/T_t} \frac{(1-\alpha_e)}{\alpha_e^2} \bigg/ (1 - e^{-\theta_v}) e^{-\theta_v} \frac{(1-\alpha_0)}{\alpha_0^2} \quad (D16)$$

In the computer programme the numerator is named as FUNRO2 (TT, ALPHA) with TT and ALPHA as arguments such that the denominator becomes FROO = FUNRO2 (1., ALPHA0) and the density is given as

$$\rho = \text{RO} = \text{FUNRO2} / \text{FROO} \quad (D17)$$

$$\text{where FUNRO2 (TT, ALPHA)} = (T_t)^{1/2} (1 - e^{-\theta_v/T_t}) e^{-\theta_v/T_t} (1-\alpha) / \alpha^2 \quad (D18)$$

The mass, energy and state equations (C2), (C3), (C4) become,

$$\rho' \theta_v' A = \rho_0 \rho \sqrt{RT_{t0}} \theta_v A^* A = m' \quad (D19)$$

$$\text{or } \rho \theta_v A = \frac{m'}{\rho_0 \sqrt{RT_{t0}} A^*} = m$$

$$h' + \frac{\theta_v'^2}{2} = R T_{t0} (h + \frac{\theta_v^2}{2}) = h_0 \text{ or } h + \frac{\theta_v^2}{2} = \frac{h_0}{R T_{t0}} = h_0 \quad (D20)$$

$$\rho_0 \rho = \rho' = \rho' R T_t' (1+\alpha) = \rho_0 \rho R T_{t0} T_t (1+\alpha) \quad (D21)$$

$$\text{or } \rho = \rho T_t (1+\alpha) \frac{\rho_0 R T_{t0}}{\rho_0} = \rho T_t (1+\alpha) / (1+\alpha_0)$$

Eq. (C18) which gives the relation between α , T_t in equilibrium becomes,

$$\frac{3\alpha}{2} + 2 \log \frac{\alpha T_t'}{(1-\alpha)(1-e^{-\theta_v'/T_t'})} + (1+\alpha) \frac{\theta_v'}{T_t'} + (1-\alpha) \frac{\theta_v'/T_t'}{e^{\theta_v'/T_t'} - 1} = \text{Constant} \quad (D22)$$

Evaluating the constant at reservoir condition.

$$\text{Constant} = \frac{3\alpha_0}{2} + 2 \log \frac{\alpha_0 T_{t0}}{(1-\alpha_0)(1-e^{-\theta_v/T_{t0}})} + (1+\alpha_0) \frac{\theta_v}{T_{t0}} + (1-\alpha_0) \frac{\theta_v/T_{t0}}{e^{\theta_v/T_{t0}} - 1}$$

$$= \frac{3\alpha_0}{2} + 2 \log \frac{\alpha_0 T_{t_0}}{(1-\alpha_0)(1-e^{-\theta_v})} + (1+\alpha) \theta_0 + (1-\alpha) \frac{\theta_v}{e^{\theta_v}-1} \quad (D23)$$

Substituting Eq. (D23) for the constant in Eq. (D22),

$$\frac{3\alpha}{2} + 2 \log \frac{\alpha T_t T_{t_0}}{(1-\alpha)(1-e^{-\theta_v/T_t})} + (1+\alpha) \frac{\theta_0}{T_t} + (1-\alpha) \frac{\theta_v/T_t}{e^{\theta_v/T_t}-1} = \frac{3\alpha_0}{2} + (1+\alpha_0) \theta_0 + (1-\alpha_0) \frac{\theta_v}{e^{\theta_v}-1} + 2 \log \frac{\alpha_0 T_{t_0}}{(1-\alpha_0)(1-e^{-\theta_v})} \quad (D24)$$

Cancelling the T_{t_0} term under the logarithmic on either side, this is written as

$$\text{FUN 53 (TT, ALPHA)} = \text{FUN 53 (1., ALPHA}_0) = F_0 \quad (D25)$$

with TT and ALPHA as arguments of the function FUN 53 where

$$\text{FUN 53 (TT, ALPHA)} = \frac{3\alpha}{2} + (1+\alpha) \frac{\theta_0}{T_t} + (1-\alpha) \frac{\theta_v/T_t}{e^{\theta_v/T_t}-1} + 2 \log \frac{\alpha T_0}{(1-\alpha)(1-e^{-\theta_v/T_t})} \quad (D26)$$

and Eq. (D24) denoted by FUN 52 (TT, ALPHA) is simply

$$\text{FUN 52 (TT, ALPHA)} = \text{FUN 52 (TT, ALPHA)} - F_0 \quad (D27)$$

Similarly, Eq. (C21) for the determination of equilibrium mass flow is

$$g^2 R \left[(1+\alpha) X_\alpha - T_t X_{T_t} + \frac{h_\alpha}{R} X_{T_t} - X_\alpha \frac{h_{T_t}}{R} \right] + R^2 P X_p \left[(1+\alpha) \frac{h_\alpha}{R} - T_t \frac{h_{T_t}}{R} \right] + R^2 (1+\alpha) T_t \left[\frac{h_{T_t}}{R} - X_{T_t} \frac{h_\alpha}{R} \right] = 0 \quad (D28)$$

From (C11) and (C15), it will be seen that $\frac{h_\alpha}{R}$ and $\frac{1}{X_{T_t}} = 0$ have dimensions of temperature while from Eqs. (C12)-(C14), it will be seen that $\frac{h_{T_t}}{R}$, X_α , $P X_p$ are dimensionless. Thus the brackets in the

first and last term in Eq. (D28) are dimensionless and the bracket in the second term has dimensions of temperature, and one finds

$$g^2 R \left[(1+\alpha) X_\alpha - T_t X_{T_t} + \frac{h_\alpha}{R} X_{T_t} - X_\alpha \frac{h_{T_t}}{R} \right] + R^2 T_t P X_p \left[(1+\alpha) \frac{h_\alpha}{R} - T_t \frac{h_{T_t}}{R} \right] + R^2 T_t (1+\alpha) T_t \left[\frac{h_{T_t}}{R} - X_{T_t} \frac{h_\alpha}{R} \right] = 0 \quad (D29)$$

Here the quantities $P X_p$, X_α , X_{T_t} , $\frac{h_\alpha}{R}$, $\frac{h_{T_t}}{R}$ are given in Eqs. (C11)-(C15), with θ_α , θ_v , T_t are dimensionless quantities. Dividing Eq. (D29) throughout by $R^2 T_{t_0}$ one finds

$$g^2 \left[(1+\alpha) X_\alpha - T_t X_{T_t} + \frac{h_\alpha}{R} X_{T_t} - X_\alpha \frac{h_{T_t}}{R} \right] + P X_p \left[(1+\alpha) \frac{h_\alpha}{R} - T_t \frac{h_{T_t}}{R} \right] + (1+\alpha) T_t \left[\frac{h_{T_t}}{R} - X_{T_t} \frac{h_\alpha}{R} \right] = 0 \quad (D30)$$

which is in dimensionless form. Also $g^2 = g'^2 / R T_{t_0}$. This expression is denoted by the function FUN51 (TT, ALPHA) and the various quantities are given the following Fortran names,

$$\begin{aligned} \text{XALPHA} &= X_\alpha \\ \text{XT} &= X_{T_t} \\ \text{ROXRO} &= P X_p \\ \text{HALPHA} &= h_\alpha / R \end{aligned}$$

$$\begin{aligned} \text{HT} &= h_T / R = \text{FUNHT (ALPHA)} \\ \text{CAPZ} &= q^2 \end{aligned}$$

The other variables in Eqs. (D19)-(D21) are denoted in Fortran by

$$\begin{aligned} \text{RO} &= \rho \\ \text{U} &= \bar{u} \\ \text{AC or AREA} &= A \\ \text{H} &= h = \text{FUNH (TT, ALPHA)} \\ \text{HO} &= h_o = \text{FUNH (1., ALPHA}_o) \\ \text{P} &= p \\ \text{ALFP1} &= 1 + \alpha \\ \text{ALFM1} &= 1 - \alpha \\ \text{ALFoP1} &= 1 + \alpha_o \\ \text{ALPHEL} &= \alpha_e \text{ (local equilibrium } \alpha \text{)} \\ \text{y(1) or TT} &= T_t \\ \text{y(2) or TV} &= T_v \\ \text{y(3) or ALPHA} &= \alpha \\ \text{CURLMC} &= \dot{m} \text{ (mass flow)} \\ \text{THETAV} &= \theta_v \\ \text{THETAD} &= \theta_D = \text{THETDD}/T_{oD} = \theta'_v/T_{t_o} \\ \text{THETAR} &= \theta_r \\ \text{ToD} &= T_{t_o} \text{ (dimensions in } ^\circ\text{K)} \\ \text{PoD} &= p_o \text{ (dimensions in dynes / cm}^2\text{)} \\ \text{ROoD} &= \rho_o \text{ (dimensions gm / cm}^3\text{)} \end{aligned}$$

Partially frozen flow :-

For the partially frozen case, the mass, energy, state equations (D19) to (D21) are the same. The ρ , T_t relation given in Eq. (C25) is, after evaluation of the constant from the reservoir conditions,

$$\begin{aligned} &\log \rho' - \frac{5+\alpha}{2(1+\alpha)} \log T_t' - \frac{(1-\alpha)}{1+\alpha} \left[\frac{\theta_v'/T_t'}{e^{\theta_v'/T_t'} - 1} - \log(1 - e^{-\theta_v'/T_t'}) \right] \\ &= \log \rho_o - \frac{5+\alpha_o}{2(1+\alpha_o)} \log T_{t_o} - \frac{1-\alpha_o}{1+\alpha_o} \left[\frac{\theta_v'/T_{t_o}}{e^{\theta_v'/T_{t_o}} - 1} - \log(1 - e^{-\theta_v'/T_{t_o}}) \right] \end{aligned} \quad (\text{D31})$$

For partially frozen flow from the reservoir, the α on the left hand side in Eq. (D31) i.e. also α_o , so that the above equation can be rearranged as

$$\log \frac{\rho'}{\rho_o} - \frac{5+\alpha_o}{2(1+\alpha_o)} \log \frac{T_t'}{T_{t_o}} - \frac{1-\alpha_o}{1+\alpha_o} \left[\frac{\theta_v'/T_t'}{e^{\theta_v'/T_t'} - 1} - \frac{\theta_v}{e^{\theta_v} - 1} - \log \frac{(1 - e^{-\theta_v'/T_t'})}{(1 - e^{-\theta_v})} \right] = 0$$

$$\text{or } \log \rho = \frac{5+\alpha_o}{2(1+\alpha_o)} \log T_t - \frac{1-\alpha_o}{1+\alpha_o} \left[\varepsilon_v(T_t) - \varepsilon_v(1.0) - \log \frac{Q(T_t)}{Q(1.0)} \right]$$

$$\text{FUNRO} = \rho = \exp \left\{ \frac{5+\alpha_o}{2(1+\alpha_o)} \log T_t - \frac{1-\alpha_o}{1+\alpha_o} \left[\varepsilon_v(T_t) - \varepsilon_v(1.0) - \log \frac{Q(T_t)}{Q(1.0)} \right] \right\} \quad (\text{D32})$$

The right hand side of Eq. (D32) is denoted by RO=FUNRO (TT, ALPHA0) in Fortran and is used to evaluate ρ for partially frozen flows.

For the evaluation of the partially frozen mass flow, Eq. (C27) is

$$R g'^2 \left[\frac{k_{T_e}}{R} - (1+\alpha_0) \right] - R^2 (1+\alpha_0) T_e' \frac{k_{T_e}}{R} = 0$$

$$\text{or } g'^2 \left[\frac{k_{T_e}}{R} - (1+\alpha_0) \right] - (1+\alpha_0) T_e' \frac{k_{T_e}}{R} = 0 = \text{FUN3}(TT, \text{ALPHA0}) \quad (\text{D33})$$

Note that k_{T_e}/R is dimensionless and we have replaced g'^2 by $g'^2 R T_e$ and T_e' by $T_e' T_e$. The left hand side of Eq. (D33) is denoted in Fortran by FUN3 (TT, ALPHA0) with TT, ALPHA0 as arguments.

Nonequilibrium flow:-

In nonequilibrium flow also, the mass, energy, state equations have the same non-dimensional form given in Eqs. (D19)-(D21). The coupled ordinary differential equations for T_t , E_v or $1/T_v$, α given in Eqs. (103), (98), (97) are non-dimensionalised as follows:

Dissociational rate equation

The dissociational rate equation is

$$\frac{d\alpha}{dx} = \frac{\psi'}{g'} (V L' - 1) \quad (\text{D34})$$

where α and V are already dimensionless and ψ' is given by

$$\psi' = \frac{k_1}{m_a^2} \rho'^2 (1-\alpha+2\lambda\alpha) \alpha^2 = \frac{k_{10} \rho_0^2}{m_a^2} k_1 \rho^2 (1-\alpha+2\lambda\alpha) \alpha^2 \quad (\text{D35})$$

$$\frac{\psi'}{g'} = \frac{k_{10} \rho_0^2}{m_a^2 \sqrt{R T_{t_0}}} \cdot \frac{k_1 \rho^2}{g} (1-\alpha+2\lambda\alpha) \alpha^2 \quad (\text{D36})$$

$$\lambda = \lambda' / \ell \quad (\text{D37})$$

where ℓ is a characteristic length and

$$\begin{aligned} L = L' &= \frac{m_a}{2\rho_0} \cdot K_C' \frac{(1-\alpha)}{\alpha^2} = \frac{m_a}{2\rho_0} K_{C_0} \frac{K_C}{\rho} \frac{1-\alpha}{\alpha^2} \\ &= \frac{\alpha_0^2}{1-\alpha_0} \frac{K_C}{\rho} \frac{1-\alpha}{\alpha^2} \end{aligned} \quad (\text{D38})$$

since $\frac{m_a}{2\rho_0} K_{C_0} = \frac{\alpha_0^2}{1-\alpha_0}$

Thus

$$\frac{d\alpha}{dx} = \frac{1}{\ell} \frac{d\alpha}{dx} = \frac{k_{10} \rho_0^2}{m_a^2 \sqrt{R T_{t_0}}} \frac{k_1 \rho^2}{g} (1-\alpha+2\lambda\alpha) \alpha^2 \left[\frac{\alpha_0^2}{1-\alpha_0} V \frac{K_C}{\rho} \frac{1-\alpha}{\alpha^2} - 1 \right] \quad (\text{D39})$$

or

$$DALDX = \frac{d\alpha}{dx} = \frac{\gamma}{\beta} (VL - 1) \quad (D40)$$

where

$$ZETA = \gamma = \frac{L k_n p_0^2}{m_a^2 \sqrt{R T_{t_0}}} \quad (D41)$$

$$PSI = \gamma = k_n p^2 (1 - \alpha + 2\lambda \alpha) \alpha^2 \quad (D42)$$

$$L = \frac{\alpha_0^2}{1 - \alpha_0} \cdot \frac{K_c}{p} \cdot \frac{1 - \alpha}{\alpha^2} \quad (D43)$$

and

$$V = \frac{Q(T_t)}{Q(T_v)} \cdot \frac{Q(T_f)}{Q(-U)} \quad (D44)$$

where Q's are given by Eq. (B21)

From Eqs. (D9) for K_c and (D18) for FRO_0 , one may note that

$$\begin{aligned} L &= \frac{\alpha_0^2}{1 - \alpha_0} \cdot \frac{K_c}{p} \cdot \frac{1 - \alpha}{\alpha^2} = \frac{\alpha_0^2}{1 - \alpha_0} \cdot \frac{(T_t)^{1/2} (1 - e^{-\theta_1/T_t}) e^{-\theta_2/T_t}}{(1 - e^{-\theta_1}) e^{-\theta_2}} \cdot \frac{1 - \alpha}{p \alpha^2} \\ &= \frac{(T_t)^{1/2} (1 - e^{-\theta_1/T_t}) e^{-\theta_2/T_t}}{FRO_0} \cdot \frac{(1 - \alpha)}{p \alpha^2} \\ &= \frac{(T_t)^{1/2} e^{-\theta_2/T_t}}{FRO_0 Q(T_t)} \cdot \frac{1 - \alpha}{p \alpha^2} = \frac{K_{c_1}}{FRO_0} \cdot \frac{(1 - \alpha)}{p \alpha^2} \end{aligned} \quad (D45)$$

Note that $Q(T_t)$ is nothing but the vibrational partition function obtained by replacing T_v by T_t and is equal to $(1 - e^{-\theta_1/T_t})$. In Eq. (D40) V and L occur as a product. It was found in the calculations that for $T_t < 0.4$, V reaches the capacity of the computer i. e. $V > 10^{38}$ and K_{c_1} reaches the other extreme, i. e. $K_{c_1} < 10^{-38}$. Thus the product VL was calculated by different methods for $T_t \geq 0.4$, namely

$$(I) \text{ for } T_t > 0.4 \quad CAPL = PH1 * \sqrt{T_t} e^{-\theta_2/T_t} (1 - \alpha) / p \alpha^2 \quad (D46)$$

$$\text{where } PH1 = 1/FRO_0 \quad (D47)$$

$$\text{and } CAPV = Q(T_f) / Q(T_v) Q(-U) \quad (D48)$$

$$(II) \text{ for } T_t < 0.4, \quad (D49)$$

$$CAPL = PH1 * \sqrt{T_t} (1 - \alpha) / p \alpha^2$$

$$CAPV = e^{-\theta_2/T_t} \cdot Q(T_f) / Q(T_v) Q(-U) \quad (D50)$$

The λ occurring in Eq. (D42) which takes into account the relative efficiencies of atoms and molecules in causing dissociation is given the Fortran name FLABDA and its value given by Eq. (B83) is

$$\text{FLABDA} = \bigwedge = 35. \frac{T_t}{\theta_v} \quad (\text{D51})$$

Vibrational relaxation equation:-

The vibrational relaxation equation is

$$\frac{d\varepsilon'_v}{dx} = \frac{\varepsilon'_\infty - \varepsilon'_v}{\delta' \tau'_v} - \frac{\psi' \nu L' (\bar{E} - \varepsilon'_v)}{\delta' (1-\alpha)} + \frac{\psi' (\bar{G} - \varepsilon'_v)}{\delta' (1-\alpha)} \quad (\text{D52})$$

The various energy terms ε'_∞ , ε'_v , \bar{E} , \bar{G} have dimensions of RT_{t_0} while δ'/ψ and $\delta' \tau'_v$ have dimensions of length and L' is dimensionless. Thus dividing the above equation throughout by ℓ/RT_{t_0} to make it non-dimensional, one obtains

$$\frac{d\varepsilon_v}{dx} = \frac{\ell(\varepsilon_\infty - \varepsilon_v)}{\delta' \tau'_v} - \frac{\ell \psi' \nu L' (\bar{E} - \varepsilon_v)}{\delta' (1-\alpha)} + \frac{\ell \psi' (\bar{G} - \varepsilon_v)}{\delta' (1-\alpha)} \quad (\text{D53})$$

In conformity with the dissociational rate equation

$$\frac{\ell \psi'}{\delta'} = \frac{\gamma \psi}{\delta}, \quad L' = L \quad (\text{D54})$$

and

$$\delta' \tau'_v / \ell = \sqrt{RT_{t_0}} \tau_{v_0} \cdot \delta \tau_v / \ell \quad (\text{D55})$$

where τ_{v_0} is evaluated at reservoir conditions. Taking γ as a common factor, one has

$$\text{DEPDx} = \frac{d\varepsilon_v}{dx} = \gamma \left\{ \eta \frac{\varepsilon_\infty - \varepsilon_v}{\delta \tau_v} - \frac{\psi \nu L (\bar{E} - \varepsilon_v)}{\delta (1-\alpha)} + \frac{\psi (\bar{G} - \varepsilon_v)}{\delta (1-\alpha)} \right\} \quad (\text{D56})$$

$$\text{where } \text{ETA} = \eta = \ell / \gamma \tau_{v_0} \sqrt{RT_{t_0}} \quad (\text{D57})$$

Eq. (D56) is used in the calculations.

As was already indicated in section 5.2, the vibrational energy and partition function were calculated by summing over the various energy levels. The quantities \bar{E} , \bar{G} , ε_∞ , $Q(T_t)$, $Q(T_f)$ and $Q(-U)$ were also calculated in this manner.

We have

$$e_{vib} = R \sum E'_j / k e^{-E'_j / k T_v} / Q_{vib} \quad (\text{D58})$$

and

$$f'' = Q_{vib} = \sum e^{-E'_j / k T_v} \quad (\text{D59})$$

where E'_j is the energy with dimensions in ergs and k is the Boltzmann constant, m is the mass of the atom in gm. E'_j can be expressed in dimensions cm^{-1} as

$$E'_j = ch E''_j \quad (\text{D60})$$

where E''_j whose Fortran name is EJPP is given in Eq. (114) and has dimensions cm^{-1} . Here c is the speed of light and h Planck's constant. In the computer programme, E'_j / k was replaced by θ'_{vj} such that

$$\theta'_{vj} = \frac{E'_j}{k} = \frac{ch}{k} E''_j \quad (\text{D61})$$

Non-dimensionalising by T_{t_0} one has

$$\text{THETVJ} = \theta_{vj} = \frac{\theta_{vj}}{T_{t_0}} = \frac{ch}{R T_{t_0}} E_j'' = \text{FACTOR} * E_j'' \quad (\text{D62})$$

which is denoted in Fortran by THETVJ. With $j=1$, one recovers θ_v which is the non-dimensionalised characteristic vibrational temperature.

$$\text{THETA V} = \theta_v = \theta_{v1} = \frac{\theta_{v1}}{T_{t_0}} = \frac{ch}{R} \cdot \frac{E_1''}{T_{t_0}} \quad (\text{D63})$$

By this non-dimensionalisation, one has

$$\mathcal{E}_v = \frac{e_{vib}}{R T_{t_0}} = \sum \theta_{vj} e^{-\theta_{vj}/T_v} / Q(T_v) = EPSTV \quad (\text{D64})$$

and

$$Q(v) = Q_{vib} = \sum e^{-\theta_{vj}/T_v} = QTV \quad (\text{D65})$$

$$\text{Similarly } \mathcal{E}_o = \sum \theta_{vj} e^{-\theta_{vj}/T_t} / Q(T_t) = EPSTT \quad (\text{D66})$$

$$\bar{E} = \sum \theta_{vj} e^{-\theta_{vj}/T_f} / Q(T_f) = \bar{E}BAR \quad (\text{D67})$$

$$\bar{G} = \sum \theta_{vj} e^{\theta_{vj}/U} / Q(-U) = \bar{G}BAR \quad (\text{D68})$$

$$Q(T_t) = \sum e^{-\theta_{vj}/T_t} = QTT \quad (\text{D69})$$

$$Q(T_f) = \sum e^{-\theta_{vj}/T_f} = QTF \quad (\text{D70})$$

$$Q(-U) = \sum e^{\theta_{vj}/U} = QTU \quad (\text{D71})$$

The quantity U which occurs in the efficiency factor P_j is also non-dimensionalised by T_{t_0} , that is

$$U = U' / T_{t_0} \quad (\text{D72})$$

Since only two values of U are used, namely $U = \infty$ and $U = \theta_D / 6$ the reciprocal of U is written as

$$\text{CAPUR} = \text{CAPU} = \text{UFACT} / \text{THETAD} \quad (\text{D73})$$

Where UFACT is zero or six depending on whether nonpreferential or preferential model is used. This inverse value $1/U$ is used since it always occurs in the equations in that form.

The second term on the right hand side of Eq. (D56) is slightly changed for $T_t < 0.4$ because of the change in CAPL and CAPV indicated in Eqs. (D49), (D50), by redefining \bar{E} and $Q(T_f)$ given in Eqs. (D67) and (D70) as follows:

$$\bar{E}BAR = \bar{E} = \sum Q_{vj} e^{-\theta_{vj}/T_f} \cdot e^{-\theta_D/T_t} \quad (\text{D74})$$

and $QTF = Q(T_f) = \sum e^{-\theta_0/T_f} e^{-\theta_1/T_f} \text{ for } T_f < 0.4$ (D75)

The second term in Eq. (D56) is rewritten as

$$\frac{\psi_{VL}(\bar{E}-E_v)}{g(1-\alpha)} = \frac{\psi}{g(1-\alpha)} \left(\frac{EBAR}{Q(T_v)Q(U)} - E_v \cdot CAPL \right) \text{ for } T_f < 0.4 \quad (D76)$$

Also, Eq. (D56) is written for the vibrational temperature, instead of vibrational energy in the form

$$DTVRDX = \frac{d(1/T_v)}{dx} = DEPDx/DEDTc \quad (D77)$$

where DEPDx is given in Eq. (D56) and the Fortran name DEDTC means

$$DEDTc = \frac{dE_v}{d(1/T_v)} \quad (D78)$$

This occurs since E_v is a function of $1/T_v$. The quantity DEDTC in Eq. (D77) was also calculated in the subroutine SUMEJ along with E_v , $Q(T_v)$. The variable TVREC = $1/T_v$ is used since it always occurs in the equations in that form. So, also, since T_f is calculated from

$$\frac{1}{T_f} = \frac{1}{T_v} - \frac{1}{T_t} - \frac{1}{U} \quad (D79)$$

the variable TFREC = $1/T_f$ is used in all calculations.

Equation for T_t :-

The differential equation for T_t' as given in Eq. (103) is

$$\frac{dT_t'}{dx} = \frac{g^2}{(1-M_f^2) \frac{7+3\alpha}{2} R} \left\{ \frac{1}{A'} \frac{dA'}{dx} - \frac{1}{1+x} \frac{dx}{dx} + \left(\frac{1}{T_t(1+\alpha)} - \frac{R}{g^2} \right) \left[\left(\frac{3}{2} T_t' - \frac{E_v + \theta_0}{R} \right) \frac{dE_v}{dx} + (1-\alpha) \frac{dE_v/R}{dx} \right] \right\} \quad (D80)$$

which is non-dimensional form is simply,

$$DTDX = \frac{dT_t}{dx} = \frac{g^2}{(1-M_f^2) \frac{7+3\alpha}{2} R} \left\{ \frac{1}{A} \frac{dA}{dx} - \frac{1}{1+x} \frac{dx}{dx} + \left(\frac{1}{T_t(1+\alpha)} - \frac{R}{g^2} \right) \left[\left(\frac{3}{2} T_t - \frac{E_v + \theta_0}{R} \right) \frac{dE_v}{dx} + (1-\alpha) \frac{dE_v/R}{dx} \right] \right\} \quad (D81)$$

where $\frac{1}{A} \frac{dA}{dx}$ are given by Eqs. (D40) and (D56) and $\frac{dE_v}{dx}$ is calculated in subprogramme FUNA and is given the Fortran name DABYA

$$DABYA = \frac{1}{A} \frac{dA}{dx} \quad (D82)$$

The derivatives $\frac{dT_t}{dx}$, $\frac{dx}{dx}$ and $\frac{d(1/T_v)}{dx}$ are also denoted by YPRIME (1, 2, 3) respectively.

All these equations are written in subprogramme DERIV7, which also evaluated the following further quantities.

Local Equilibrium α :-

In all nonequilibrium calculations, the evaluation of the atom mass fraction in equilibrium with the local pressure or density and temperature is of interest to give a measure of the nonequilibrium. The α so calculated could be different depending on whether one uses p , T_t or P , T_t for its computation; this was pointed out by Clarke (Ref. 41). In these calculations the α is based on p , T_t and is given by the equation

$$\text{ALPHEL} = \alpha_{el} = \left[1 + p \cdot (1 + \alpha_0) \cdot Q(T_t) \cdot \text{FRO}_0 \cdot \exp(\theta_0/T_t) / T_t^{1.5} \right]^{-1/2} \quad (\text{D83})$$

which was obtained by replacing p from Eq. (D16) by the state equation. The expression for FRO_0 as given in Eq. (D18) is

$$\text{FRO}_0 = Q(T_t = 1.0) \cdot e^{-\theta_0/T_t} \cdot (1 - \alpha_0) / \alpha_0^2 \quad (\text{D84})$$

where α_0 is the value in the reservoir and p , T_t are local values.

Relaxation lengths:-

Vibrational and dissociational relaxation lengths were also computed for studying the effect of the dissociation models on these. They are defined as

Vibrational

$$\text{VERL} = \varepsilon_0 - \varepsilon_v / \frac{d\varepsilon_v}{dx} \quad (\text{D85})$$

which takes into account the effect of dissociation and recombination;

$$\text{VERL1} = \ell \cdot T_v \quad (\text{D86})$$

which does not take into account the dissociation and recombination.

Dissociational

$$\text{DRL} = (\alpha_{el} - \alpha) / \frac{d\alpha}{dx} \quad (\text{D87})$$

which takes into account the vibrational nonequilibrium and

$$\text{DRL1} = \ell / \gamma \quad (\text{D88})$$

which does not take this into account.

Rate constants and coupling factor:-

Also, the rate constants k'_v , k'_{deg} , k_{deg} and the ratio $V = k'_{deg} / k_{deg}$ were calculated, their Fortran names being

$$\text{SMKR1} = k'_n = k_n \cdot k_{n0} \quad (\text{D89})$$

$$\text{SMKDEQ} = k'_{deg} = k'_c \cdot k'_i \quad (\text{D90})$$

$$\text{SMKDNQ} = k'_{dneq} \quad (\text{D91})$$

$$\text{COFAC} = k'_{dneq} / k'_{deg} \quad (\text{D92})$$

Calculations for flow past the deflection plate:

The flow past the deflection plate is calculated for frozen flow through the Prandtl-Meyer fan by the equation,

$$\theta + \tan^{-1} \sqrt{M_f^2 - 1} - \sqrt{\frac{\Gamma_f + 1}{\Gamma_f - 1}} \tan^{-1} \sqrt{\frac{\Gamma_f - 1}{\Gamma_f + 1}} \sqrt{M_f^2 - 1} = \text{Constant} \quad (\text{D93})$$

where θ is the flow deflection angle, M_f is frozen Mach number, and

$$\Gamma_f = \frac{7 + 3\alpha}{5 + \alpha} \quad (\text{D94})$$

where α is the value upstream of the deflection plate, that is at the end of the primary nozzle. The constant in Eq. (D93) is evaluated at the same point. Eq. (D93) is written in subprogramme FUNPM. Once the Mach number behind the Prandtl-Meyer fan is evaluated from Eq. (D93) the other flow variables T_t , ρ , P , g are calculated from isentropic relations in which Γ_f is used for the isentropic index.

The Fortran names for these various quantities are:

$$\text{CME1} = M_f \text{ (behind P. M. fan)} \quad (\text{D95})$$

$$\text{CME1 2} = M_f^2 \text{ (before P. M. fan)} \quad (\text{D96})$$

$$\text{GF} = \Gamma_f \quad (\text{D97})$$

T_f , ρ , P , g were given the subscripts E1 for their values behind the P.M. fan, i.e.

$$\begin{aligned} \text{TE1} &= T_{te1} \\ \text{ROE1} &= \rho_{e1} \\ \text{PE1} &= P_{e1} \\ \text{UE1} &= g_{e1} \end{aligned} \quad (\text{D98})$$

Test Section Conditions

Inviscid Results:-

The conditions in the test section were calculated starting from T_{e1} , ρ_{e1} , P_{e1} , g_{e1} under the frozen flow assumption, thus using the isentropic formulae. A new mass flow for the gas entering the terminal nozzle is evaluated with ρ_{e1} , g_{e1} and A_{e1} the entrance cross-section and is given the Fortran name CURLMI, namely

$$\text{CURLMI} = \rho_{e1} \cdot g_{e1} \cdot A_{e1} \quad (\text{D99})$$

The energy equation was slightly modified by removing the vibrational and dissociational terms from the enthalpy expression and writing

$$(7+3\alpha)T_t + q^2 = (7+3\alpha)T_{te} + q_e^2 = h_{c1} = HC1 \quad (D100)$$

where HC1 is the Fortran name for h_{c1} . The evaluation of T_t in test section denoted by TE3 is done by the use of Eqs. (D99), (D100) and state equation and the isentropic relation between T_{e3} and T_{e1} . This is written in subprogramme FUNT.

Boundary layer corrections:-

From these inviscid results and the formula for δ^* , the boundary layer displacement thickness given in Eq. (108) δ^* was calculated and a new area was evaluated taking the boundary layer into account and the evaluation of T_{e3} was repeated until the difference between two successive values of T_{e3} and that of δ^* was less than 10^{-5} . The Fortran names occurring in these calculations are

$$TR = \text{Reference temperature} \quad (D101)$$

$$REYR = \text{Reference Reynolds number} \quad (D102)$$

$$DELSTR = \delta^* \quad (D103)$$

$$TMC = \text{test section frozen Mach number} \quad (D104)$$

The test section values of T_t , f , p , q are given subscript e3, i.e.

$$\begin{aligned} TE3 &= T_t) \\ ROE3 &= f) \\ PE3 &= p) \\ UE3 &= q) \end{aligned} \quad \text{in test section} \quad (D105)$$

Details of integration procedure in the primary nozzle:-

SUBROUTINE TEST 7:

As was already discussed in some detail in section 5.3, for all calculations starting upstream of the geometrical throat, one has to evaluate the nonequilibrium mass flow and also jump through the critical point. This is accomplished by subprogramme TEST 7. The differential equation for T_t is

$$\frac{dT_t}{dx} = \frac{q^2}{(1-M_f^2) \frac{7+3\alpha}{2}} \left\{ \frac{1}{A} \frac{dA}{dx} - \frac{1}{1+\alpha} \frac{d\alpha}{dx} + \left(\frac{1}{(7+3\alpha)T_t} - \frac{1}{q^2} \left[\frac{1}{2} T_t - \epsilon_v + \theta \right] \frac{d\alpha}{dx} + (1-\alpha) \frac{de_v}{dx} \right) \right\} \quad (D106)$$

$$= -2q^2 \frac{SUM}{DIFF} \quad (D107)$$

$$\text{where } DIFF = 1 - M_f^2 \quad (D108)$$

$$\text{and } SUM = \text{numerator in brackets } / (7+3\alpha) \quad (D109)$$

For an expansion from the reservoir T_t decreases and thus $dT_t/d\chi$ is negative. But until $M_f=1$, DIFF is positive, thus SUM is negative initially. For the flow to expand beyond $M_f=1$, $\frac{dT_t}{d\chi}$ should still remain negative, but for $M_f > 1$, DIFF is negative and thus SUM should be positive. In other words DIFF changes from positive to negative in passing through $M_f=1$ and SUM from negative to positive. Both these changes should happen for the same χ which is called the critical point. However, if SUM becomes positive before M_f reaches unity, one obtains subsonic flow which is not of interest. If DIFF becomes negative before SUM becomes positive, the calculations oscillate. When SUM becomes positive first, the mass flow is increased by changing the value of FACMNE as indicated in Section 5.3. In the opposite case FACMNE is decreased until finally the values of FACMNE for subsonic and oscillatory results differ in their last significant figure used in calculations, which here is the eighth figure. In this final stage, the values of χ , T_t , T_v , α are increased by a small amount at the point where SUM reaches its maximum. All these are written in subprogramme TEST 7 and the various Fortran names are:

FACMNE	= M_{neg} / M_{eg}
FUP	= Upper limit on Facmne
FDOWN	= Lower limit on Facmne
XRE	= Restarting χ if Facmne is modified
XADD	= Amount by which χ is jumped at critical point
DY(1, 2, 3)	= Amount by which T_t , α , T_v are jumped at critical points.
SUMOLD	= value of SUM in previous step to find where SUM reaches maximum.
EPSIL1	= the amount by which SUM differs from zero, at the time of jumps.
KAP	= 1, 2, 3 indicating if DIFF is -ve, 0, or +ve respectively.
NOVER	= number of iterations of changing Facmne.

SUBROUTINE INTEGR:

As was indicated at the beginning of this appendix, the computer programme contained a mechanism for progressive increase of integration step size as the integration proceeded downstream. This was contained in subprogramme INTEGR. This was achieved as follows:-

First the integration was carried out with a step size $H=HX$ where HX is input value and then the same calculations were repeated in two half steps, i.e. $HALF=H/2$. These integrations were carried out by library tape subroutine DEQ which is based on a fourth order Runge-Kutta method. If the difference for T_t , T_v , α between these two computations was greater than a given amount R2, the step size is decreased by a factor R4, i.e. a new H is taken such that $H=H*R4$. If the number of times of this consecutive reductions in step size is greater than IR6, the calculations were stopped. This happens in one of two cases: (1) if the flow is extremely close

to equilibrium or (2) if the critical point is reached. In case (1), the non-equilibrium calculations are started further downstream and in the later case the calculations are either started with a new facmne or the jump conditions are applied.

If the difference between the full and half-step calculations was less than a value R1, for IR5 consecutive steps, the step size was increased by a factor R3, i. e. $H=H*R3$.

This subroutine also controls the interval of printing results and stops the calculations when more than a certain time TIMEUP was used or if the total number of steps KSTEP is greater than a given number of steps NSTEPS or if χ reaches its final value XLIMIT.

Some of the other Fortran names which occur in this subroutine are:

NDEGR	=	The number of differential equations to be integrated.
NSTEPR	=	Interval of printing.
KWRITE	=	The number of the integration step for which results are printed.
KINCR	=	The number of times, the difference between the full and half step calculations is within tolerance R1.
XCURR	=	The current value of χ
HTABLE	=	Integration step size at step number KTABLE.
KTABLE	=	KSTEP.

SUBROUTINE SEARCH:

This subroutine is used in the beginning of the main programme, to solve algebraic-transcendental equations for the determination of frozen and equilibrium mass flows and flow properties in the whole nozzle and also to find the initial conditions for starting nonequilibrium calculations. This is done by first taking a value of $T=ToP$ and finding the values of χ which satisfy throat conditions Eq. (D30) ALPH1 and the constant entropy condition Eq. (D24); ALPH2 and their difference is denoted by FUN 5. If either of these is not found $ToP=XRIGHT$ is decreased by a factor FACT and tried again. If this happens a number of times END, the calculations are stopped. Similarly a new value of T was taken by decreasing it by an amount DX, i. e. $XLEFT=ToP-DX$ and again ALPH1 and ALPH2 were found and again their difference found and compared with the earlier value. If they are of the same sign XLEFT is further decreased by DX until they are of different signs. This gives two limits (T_1, χ_1) , (T_2, χ_2) at which the FUN5 is of opposite signs from which the correct root (T, χ) was found by using Library tape subroutine JCP=JCPM.

For the initial conditions and equilibrium and frozen flow properties in the nozzle, the equations used are entropy and mass conservation

equation (D24) and (D19).

Other Fortran variables:

XINTGR	=	1.0 according as integration is required or not
KBOLTZ	=	Boltzmann constant
HPLANK	=	Planck constant
SMMA	=	Mass of atoms per unit mole
SMM	=	Mass of an atom
THETRD)	=	θ_N, θ_d in dimensions of temperature °K.
THETDD)		
PI	=	π
IN	=	Input tape
IOUT	=	Output tape
R	=	Gas constant referred to diatomic molecule
T0D	=	Reservoir temperature in °K
PATM	=	Reservoir pressure in atm.
Pod	=	Reservoir pressure in dynes/cm ²
Go1, Go2	=	go1, go2 statistical weight of ground energy level for atoms and molecules respectively
XSTART	=	The starting value of χ for integration
CAPMF2	=	M_1^2

The equilibrium, frozen and nonequilibrium and current values of T, P, ρ etc. are distinguished by subscripts e, f, ne, c, e. g.

TE	=	T equilibrium
TNE	=	T nonequilibrium
TC	=	T current

except in the sections containing the calculations for flow past deflection plate and test section, this is not adhered to, they being distinguished by subscripts e1, e3 as noted earlier.

SML	=	Nozzle characteristic length
D0, D1, D2	=	Constants in the expression for recombination rate constant k_r Eq. (D10)
B0, B1, B2	=	Constants in the expression for vibrational relaxation time τ_v Eq. (D11)
W1, W2, W3	=	Constants in the expression for vibrational energy E_j
ALPHA1)	=	Limits on α for solving algebraic-transcendental equations (D24), (D30)
ALPHA2)		
TF1, TF2	=	Limits on T for frozen mass flow evaluation
TFI1, TFI2	=	Limits on T for frozen flow calculations
A(1)-A(26)	=	Coefficients in the polynomial fits for Area
E(1)-E(F)	=	Limits on χ where different fits are made for Area

Order of input data:

The input data was always supplied through a F Format, except for card (9) below where an I Format is used.

The order in which they are transmitted is for each data card:-

- (1) G01, G02, SMMA, HPLANK, BOLTZK, THETRD, THETDD
- (2) T0D, PATM
- (3) W1, W2, W3
- (4) TF1, TF2
- (5) ALPHA1, ALPHA2, TOP, FACT, END, DX
- (6) ALPHA1, ALPHA2, TOP, FACT, END, DX, XSTART, XINTGR
- (7) HX, XLIMIT
- (8) R1, R2, R3, R4, XINTER, TIMEUP
- (9) IR5, IR6, NSTEPR, NSTEPS, KLOCK, NTYPE
- (10) D0, D1, D2, B0, B1, B2, UFACT, SML
- (11) FUP, FDOWN, XRE, XADD, EPSIL, EPSIL1
- (12) A(1), A(2), A(3), A(4), A(5), A(6), A(7), A(8)
- (13) A(9), A(10), A(11), A(12), A(13), A(14), A(15), A(16)
- (14) A(17), A(18), A(19), A(20), A(21), A(22), A(23), A(24)
- (15) A(25), A(26), E(1), E(2), E(3), E(4), E(5), E(6)
- (16) E(7)
- (17) DTAU
- (18) DY(1), DY(2), DY(3)

Transmission of output data:

The output is always printed in E Format. They are printed in general eight quantities per line and the order is:

- (1) G01, G02, SMMA, HPLANK, BOLTZK, THETRD, THETDD, T0D
- (2) PATM, PI, R, SMM, To, PoD, THETAR, THETAD
- (3) EPST0, QTo, AT0, ALPHA0, ALFoP1, ALFoMI, ROod, Ho
- (4) Fo, FROo, THETAV

When frozen mass flow is calculated the next output data is

- (5) TF, UF, R0F, PF, CURLMF, CURLMC, AC, AF1
- (6) CAPMFI, AF2, CAPMF2, AE, CAPME

which are throat values for frozen flow.

When frozen flow properties in the nozzle are calculated, they are printed as:

- (7) X, AC, ROC, P, TAUUV, TAUD, TC, ALPHAC, UC, AF2, CAPMF2, AF1, CAPMF1, AE, CAPME

in one single line for any given X

Then the equilibrium throat properties are printed as:

- (8) FACT, END, DX, XSTART, TE, ALPHAE, UE, ROE
- (9) PE, CURLME, AF1, CAPMF1, AF2, CAPMF2, AE, CAPME

If equilibrium flow properties are calculated, they are printed as in line (7) above. Then the initial conditions for starting nonequilibrium calculations are printed as:

PE, CURLME, ALPHEI, UEI, ROEI, PEI, FACMNE, ALPHNE, UNE, RONE, THETAV, EPSC, DEDTC, XTPART, HALPHA, ALPHAC, UC, ROC, CAPMF2, TNE, CAPMF2, CURLMC

The results of the integration of the differential equations are started on a new page with the heading.

INTEGRATION STARTING

and the first line gives

XCURR, TT, ALPHA, TVREC, H, FACMNE

The second and third lines give

SMKR0D, ZETA, TAU0D, PHI, ETA, DENOM2, DENOM, CONST, CONST2, GBAR, QTU.

The results of integration for each 25 or 50 steps are then printed in six lines as,

STEPS, X, TT, ALPHA, TVREC, DTDX, DALDX, DTVRDX.
TV, TFREC, U, EPSTT, EPSTV, EBAR, GBAR, QTT.
QTV, QTF, QTU, CAPV, CAPZ, RO, CAPKC, CAPL.
SMKR, PSI, TAU, PART 1, PART 2, PART 3, PART 4, PART 5.
PART 6, CAPMF2, AREA, P, ALPHEL, DRL, DRLL, VTRL.
VERL, VERL1, SMKR1, SMKDEQ, SMKDNQ, COFAC, DELSTR.

The end of these integration results is indicated by

END OF RUN

and the last results are printed as above.

The next line of results printed on a new page give the results of calculations past the deflection plate and in the test section.

The first line give the values in front of the deflection plate as:

TC, UC, PC, ROC, CAPMF2, CME2, ALPHAC.

In the next two lines are printed the results past the deflection plate as:

CME1, TE1, AF, UE1, ROE1, PE1, AC1, CURLM1
HC1

The next line gives the inviscid test section conditions as:

TE3, ROE3, PE3, AE3, TMC, DELSTR, AC2

and the successive lines give the same results with boundary layer corrections applied, the last line giving the final corrected values.

In the case of calculations starting upstream of the throat, whenever FACMNE is changed or the jumps are used, the following data is transmitted at the position of END OF RUN. The line starts with:

RESTART FACMNE = (the new value) DIFF, SUM, SUMOLD

in the first case and in the later case,

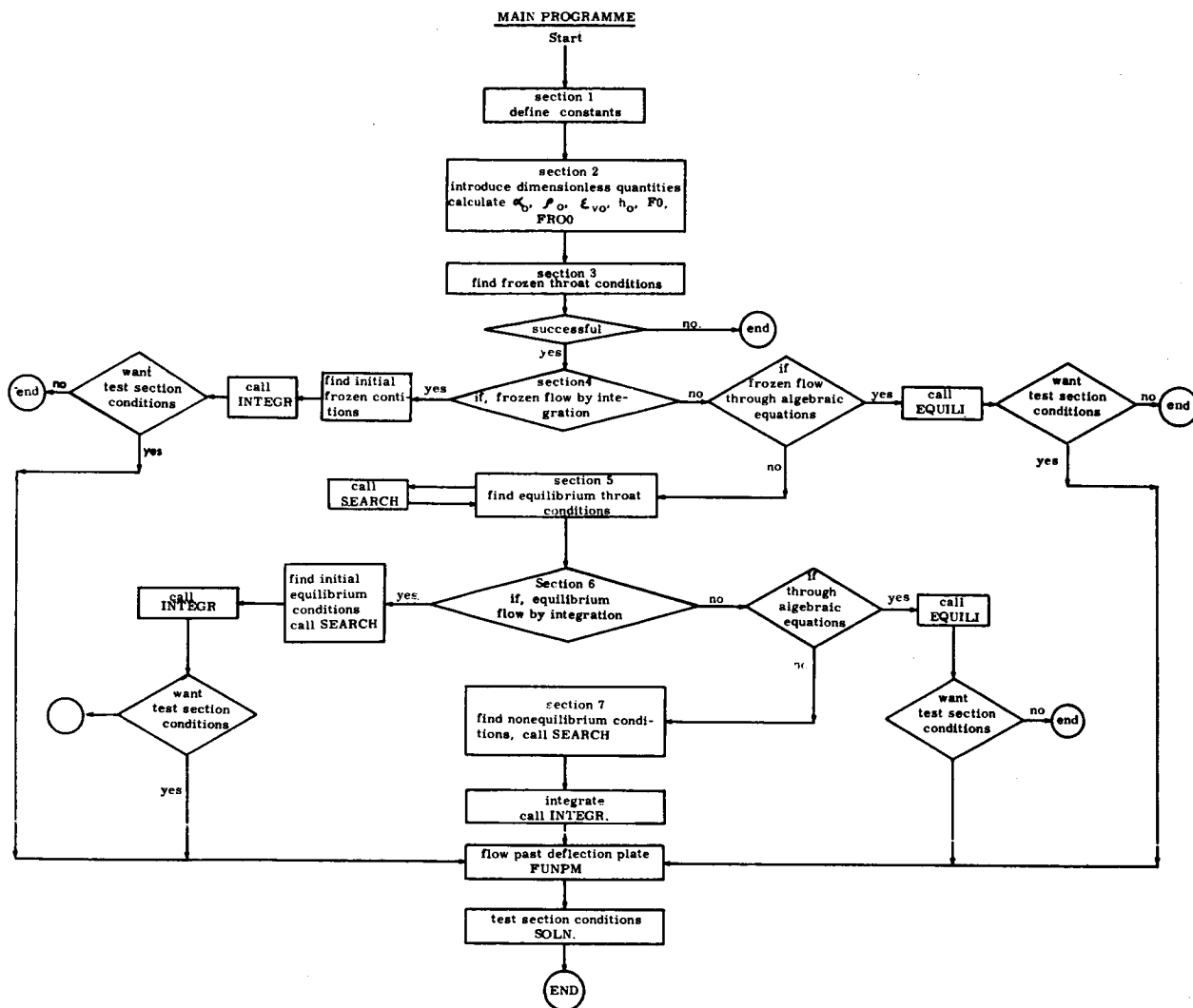
XCURR INCREMENTED XCURR, TT, ALPHA, TVR (all new), SUM,
SUMOLD.

The Fortran names of the variables of interest from the point of view of results are already given in the earlier pages. Some names like PART 1, etc. are not needed for results, but to know, if something goes wrong, what has gone wrong. For example, if any of the calculations of frozen or equilibrium mass flow or starting values or flow past deflection plate or in the test section could not be done due to the inadequacy of the limits, they are indicated by the diagnostic,

REVISE TF LIMITS (frozen mass flow)
ERROR IN SEARCH EXIT = (no.) (Equilibrium mass flow)
REVISE CME LIMITS (flow past deflection plate)
REVISE TE LIMITS (Test section conditions)

the number in equilibrium mass flow calculations indicating where the trouble arose. This may be understood by looking into subroutine SEARCH.

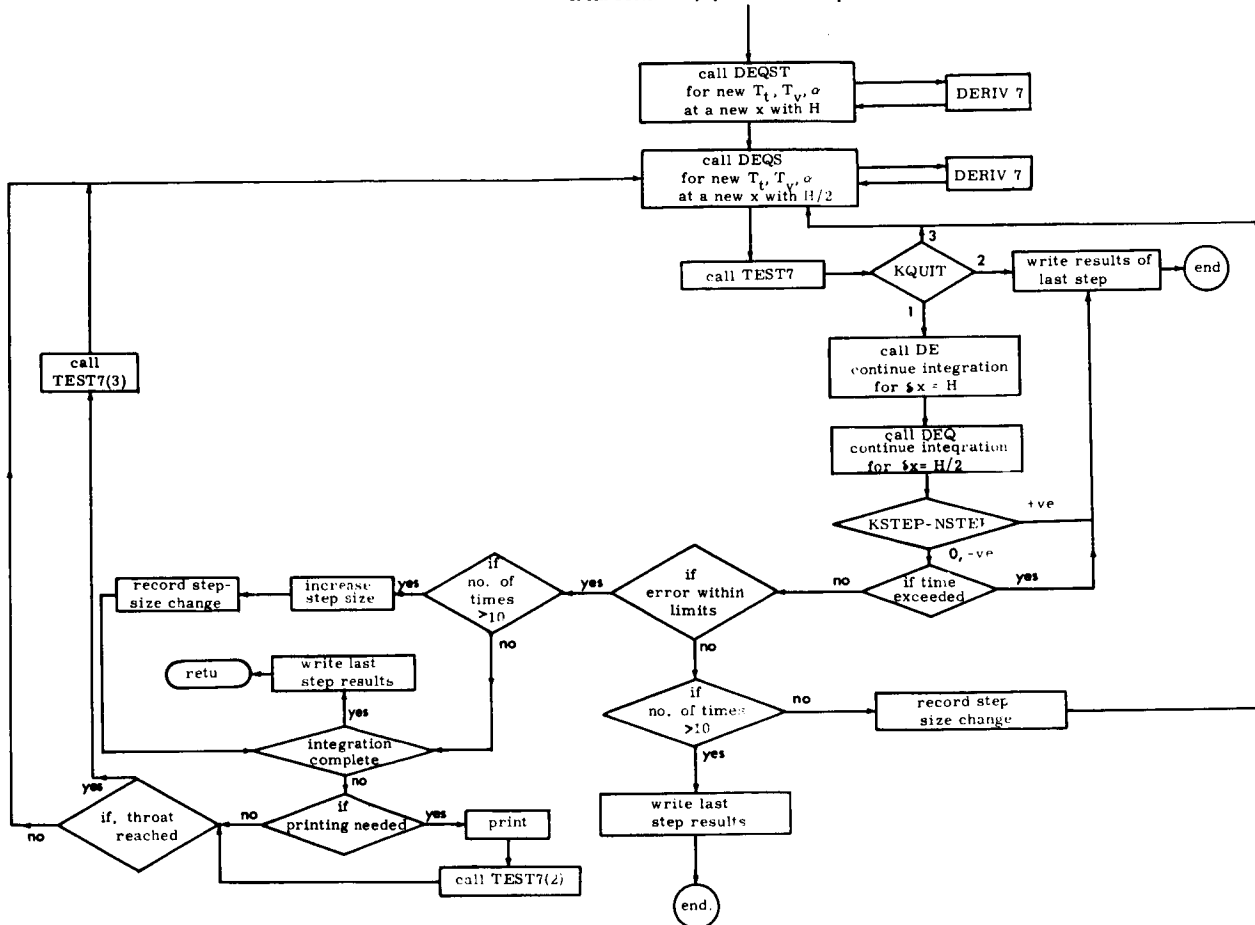
The flow diagrams in terms of Fortran names and subroutines, and the listing of the whole programme, are given in the following pages.



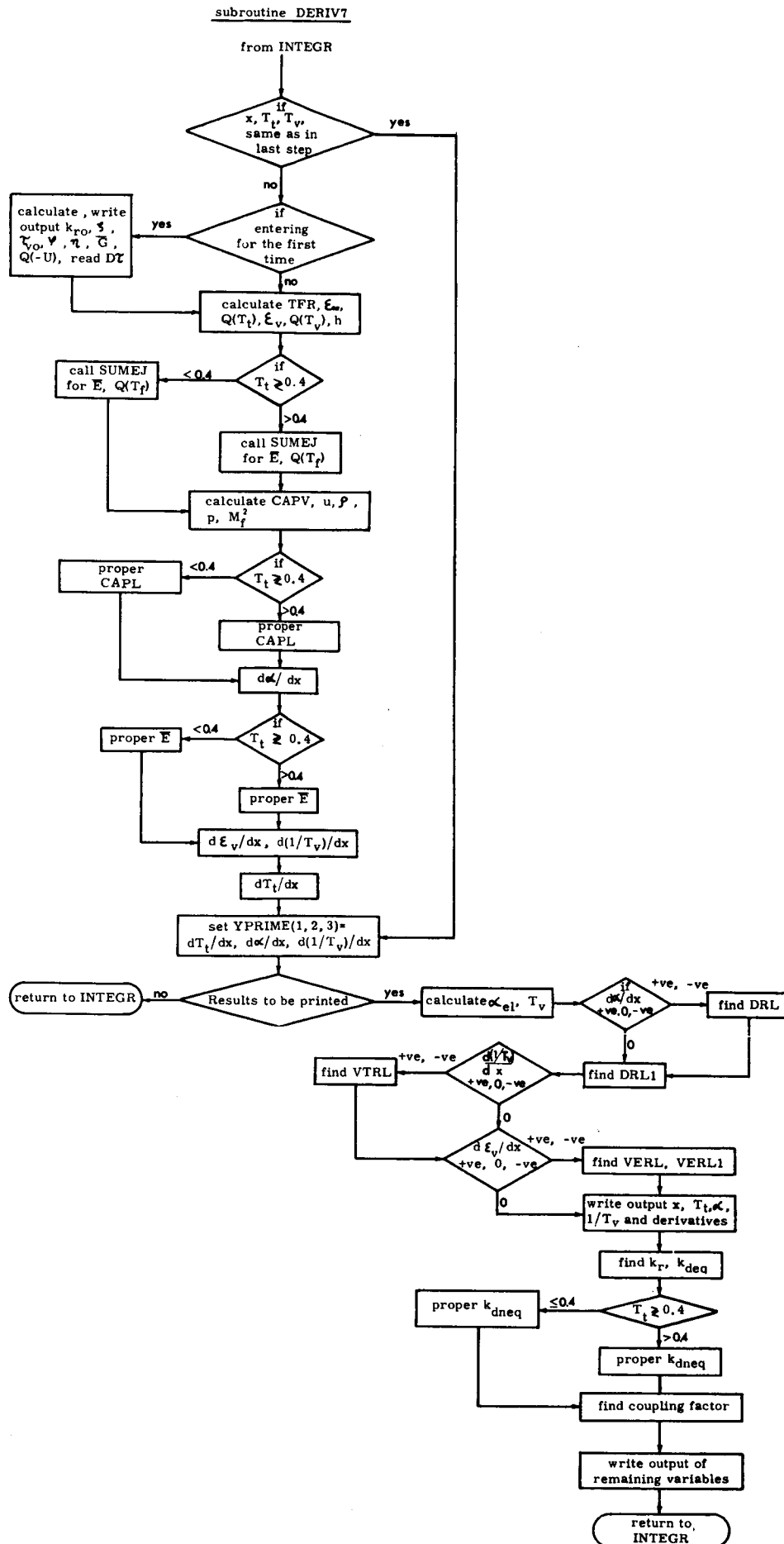
FLOW CHART D1

Subroutine INTEGR.

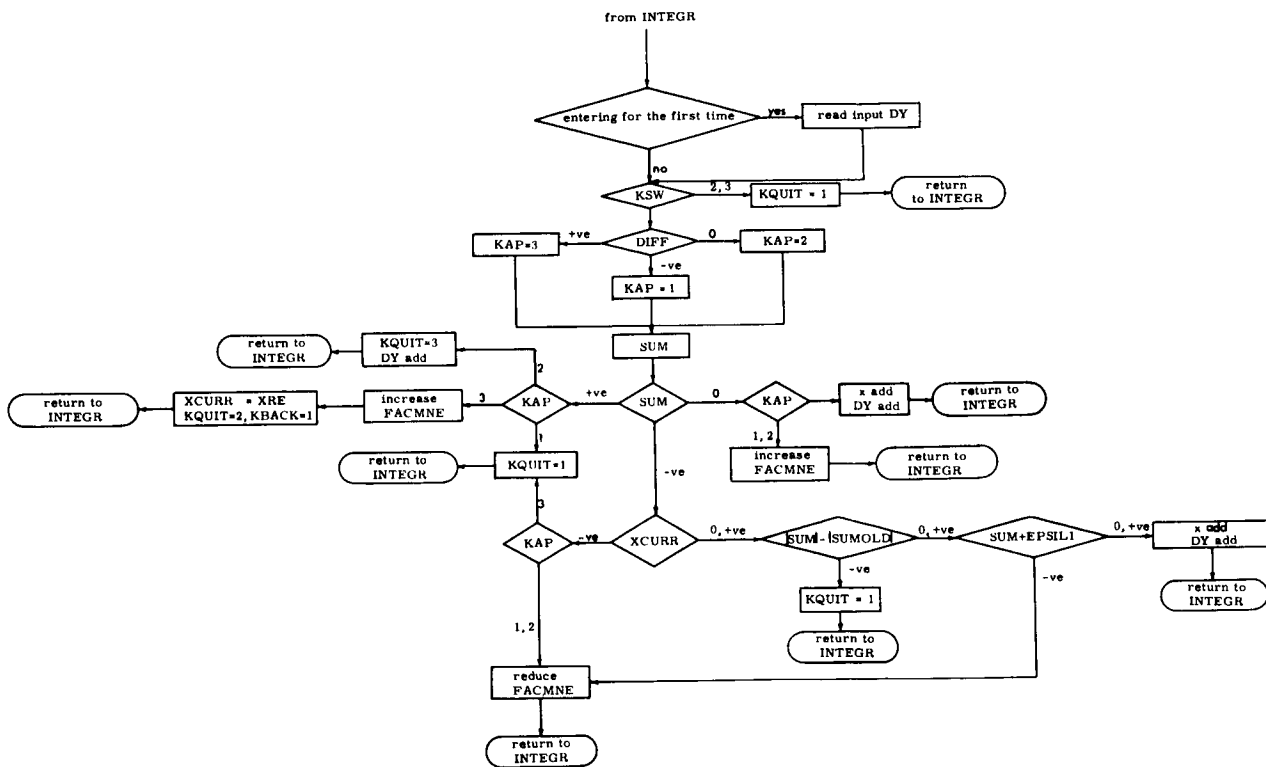
from sections 4, 6, 7 of Main Programme



FLOW CHART D2



subroutine TEST7



FLOW CHART D4

APPENDIX E

SOME COMMENTS ON THE PROBLEM OF
COUPLED VIBRATIONAL AND DISSOCIATIONAL
EQUILIBRIUM

By: J. E. Dove*

* Department of Chemistry,
University of Toronto, Toronto 5, Ontario, Canada.

The problem of the various excited electronic states of the oxygen atom and molecule is referred to rather briefly on this page. If one is concerned mainly with calculating the equilibrium properties of oxygen to a somewhat moderate degree of accuracy, then it is certainly quite true that the electronic partition functions of the oxygen molecule and atom can be treated as constant over the range 1500°K to 8000°K. Incidentally, over this temperature range, the atomic partition function actually varies from 8.38 to 9.16 and the molecular one from 3.00 to 3.68 so that the values given in the report, 8.8 and 3.3, are the averages of an appreciable spread of values.

There is, however, an additional point, which is illustrated in Fig. 13 which is taken from Ref. 44. The electronically excited molecular states have, of course, their own sets of vibrational levels. The vibrational levels of the ground state oxygen molecule are overlapped by those of the $1\Delta_g$ excited state above $v = 5$ and also by those of the $1\Sigma_g^+$ state above $v=9$. At energies close to the dissociation energy, the levels of the $3\Sigma_u^+$ state also come into consideration. The degeneracy of the ground electronic state is 3, while the degeneracies of the three excited electronic states mentioned above are 2, 1 and 3 respectively. The point of these remarks is that at equilibrium the electronically excited states will be populated, as well as the ground state, and - other things being equal - the ratio of the populations of states at a given energy will be the ratio of the electronic degeneracies. In effect, additional states are available at fairly high internal energies (electronic plus vibrational energy), and this increases the proportion of high energy molecular states which will be present at equilibrium. This has, of course, some influence on the thermal properties of the gas, though as already mentioned the effects are not extremely large. However, if, as seems likely, the higher energy states are of considerable importance in determining the rates of recombination and dissociation reactions, the effects on the kinetics could be considerable. The extent of any possible effect in an actual reaction kinetic problem will depend on whether the electronic states actually are populated under the particular experimental conditions and on the rates of population and depopulation. These rates have been studied in only a few cases, and the results, as you will know, indicate that translational-electronic energy transfer is rather slow, but that vibrational-electronic transfer is quite efficient. In such a case, the degree of electronic excitation would tend to be close to that of vibration. (However, the evidence so far is mostly concerned with the electronic excitation of metal atoms, and it is not completely certain that this can be applied directly to the electronic states of molecules.) This problem of the effect and possible participation of molecular electronic states seems to have received almost no attention in the literature, and I know of no direct experimental evidence of any effect on the kinetics. However, such evidence would be quite difficult to obtain at present.

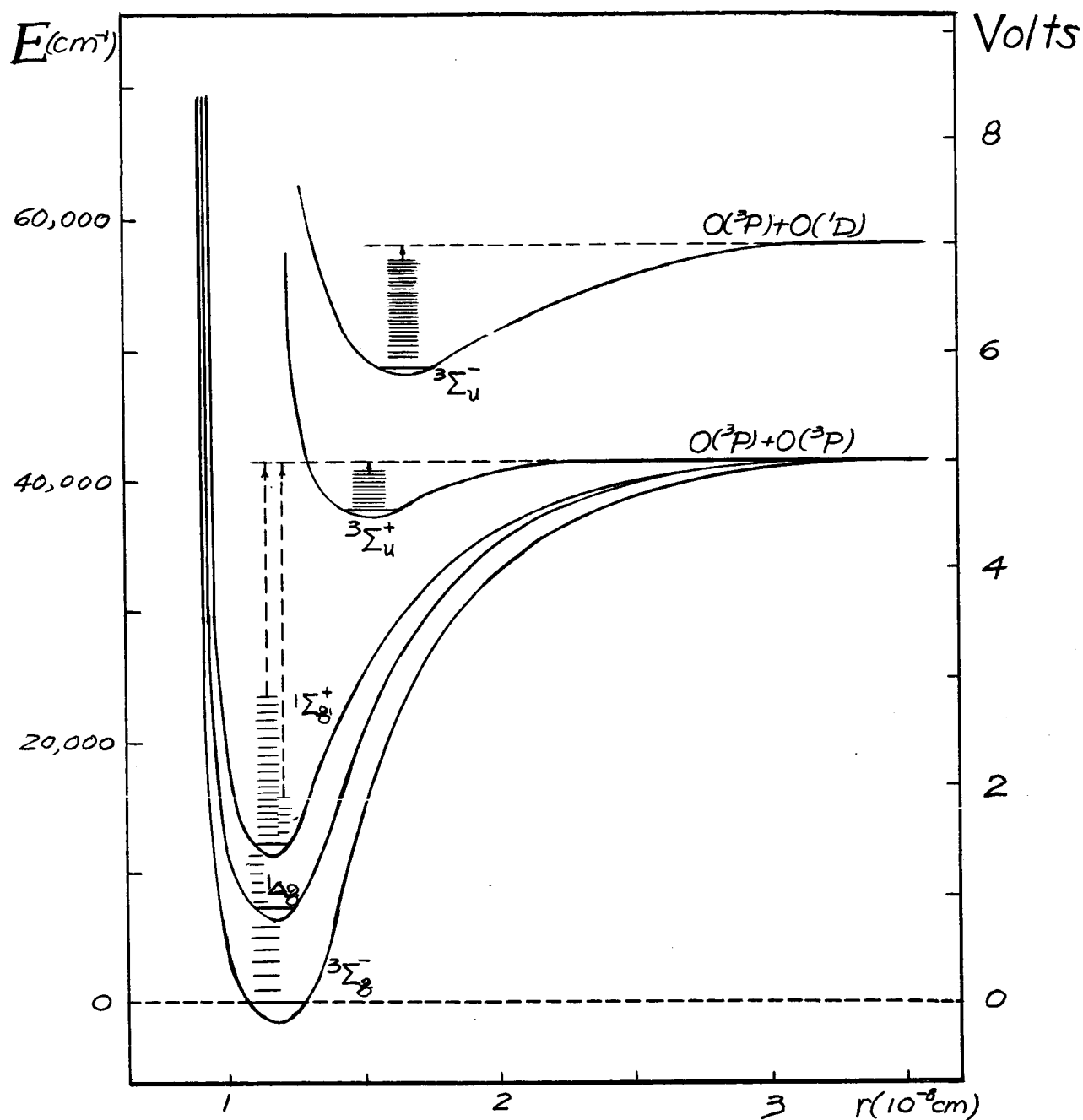


FIG. 13 Potential Curves of the Observed States of the O_2 Molecule. A number of states lying above $100,000\text{ cm}^{-1}$ (Price and Collins (571)) are not drawn, since sufficiently accurate data are not available for them. The $3\Sigma_u^+$ state has actually three more vibrational levels below the lowest one shown (see Herzberg (1044)). Taken from Reference 44, Fig. 195.

The formulation of dissociation rates which is given here is applicable to the dissociation of relatively complex molecules, but not generally of diatomic molecules. The point is that for a molecule which has a number of different modes of vibration, it can often happen that it receives sufficient internal energy to dissociate it and yet lives for many vibrational periods before actually falling apart. Then the mean lifetime of an excited molecule may be much greater than the time interval between collisions, and one may correctly consider that the activated complex consists of a single molecule.

For the dissociation of diatomic molecules, one has to consider two molecules (or a molecule and an atom) as being the activated complex. When such a molecule suffers a collision, then if it is going to fall apart at all, it will do so in a time which is comparable to the duration of a collision. In general, a diatomic molecule which has sufficient vibrational energy to enable ~~it~~ to dissociate will fall apart within the period of one vibration (2×10^{-14} sec. for O_2). This is almost always a much shorter time than the time between collisions (which even at 100 at mos. and $6000^\circ K$ is still about 10^{-11} sec.). Thus, a molecule flying freely between collisions has generally no chance of dissociating, and it is a colliding pair of molecules which constitutes the activated complex.

The formation for diatomic dissociation will then be (differing from the expressions given in the main body of the report):

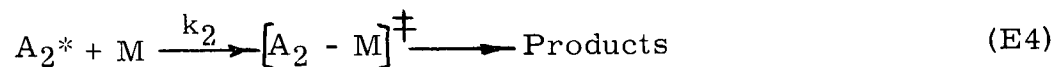


Overall rate equation:



The processes in equation (E1) are internal (vibrational) excitation and de-excitation. This formulation implies that the rate of vibrational excitation may sometimes in part determine the overall rate.

If one wants to show an activated complex, then one can re-write (E2) as



In the language of activated complex theory, this implies a transmission coefficient of unity in writing the equation in this way, that is all complexes are transformed to products.

The steady state formulation then leads to

$$\text{Rate} = - \frac{d[A_2]}{dt} = \frac{k_1 k_2}{k_{-1} + k_2} [A_2]^2$$

and $k_d = \frac{k_1 k_2}{k_{-1} + k_2} .$

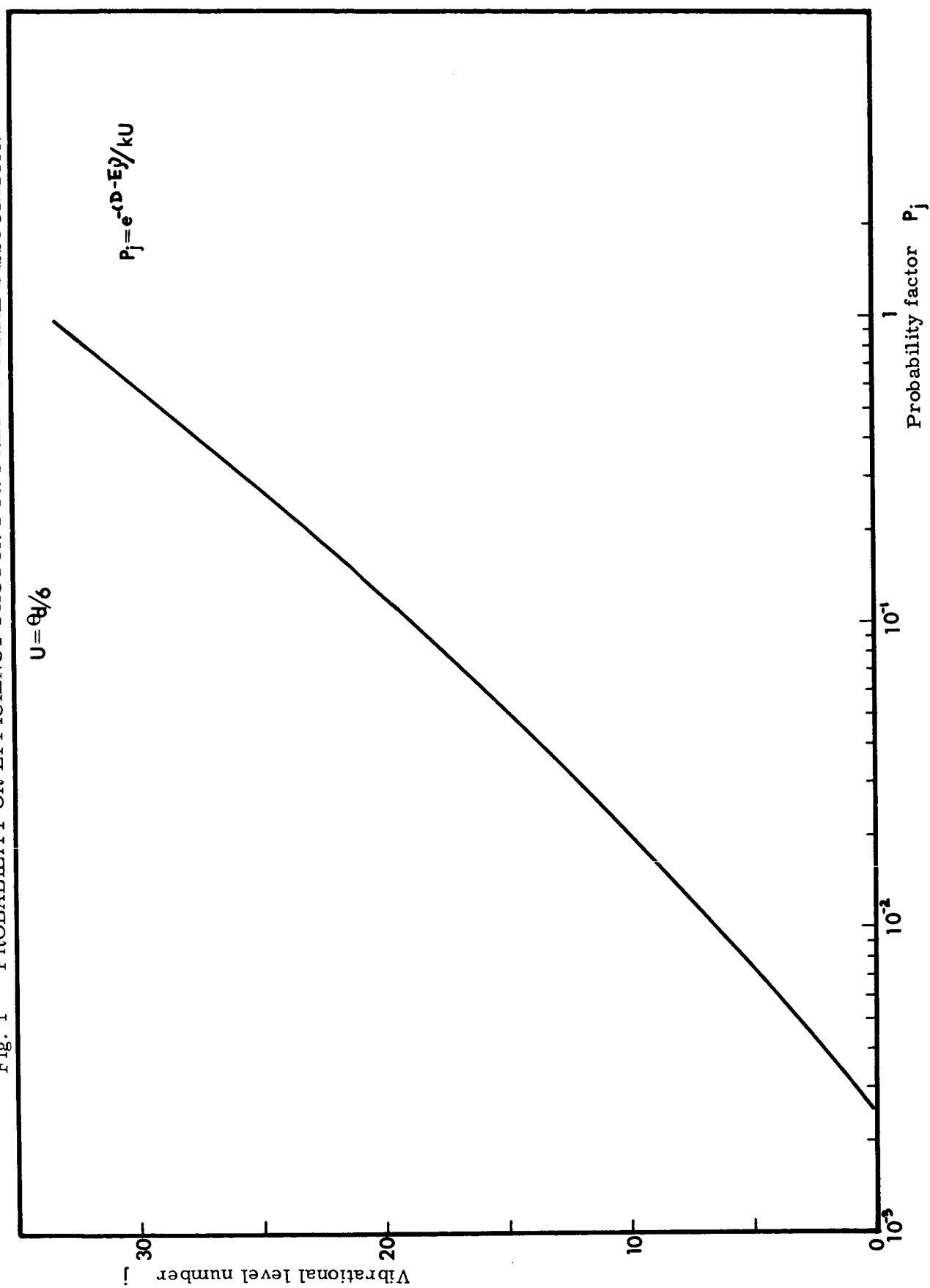
The condition for an "equilibrium" rate is that $k_{-1} \gg k_2$. Under these conditions

$$k_d = \frac{k_1}{k_{-1}} \cdot k_2 = K_1 \cdot k_2$$

where K_1 is the equilibrium constant for the processes in equation (E1).

Note that the overall rate coefficient is now not dependent on concentration in either case, and that the overall rate depends on A_2^2 . In the report, the overall equilibrium rate was proportional only to A_2 (i. e. k_d was inversely proportional to A_2 which is evidently not very reasonable.

Fig. 1 PROBABILITY OR EFFICIENCY FACTOR FOR PREFERENTIAL DISSOCIATION



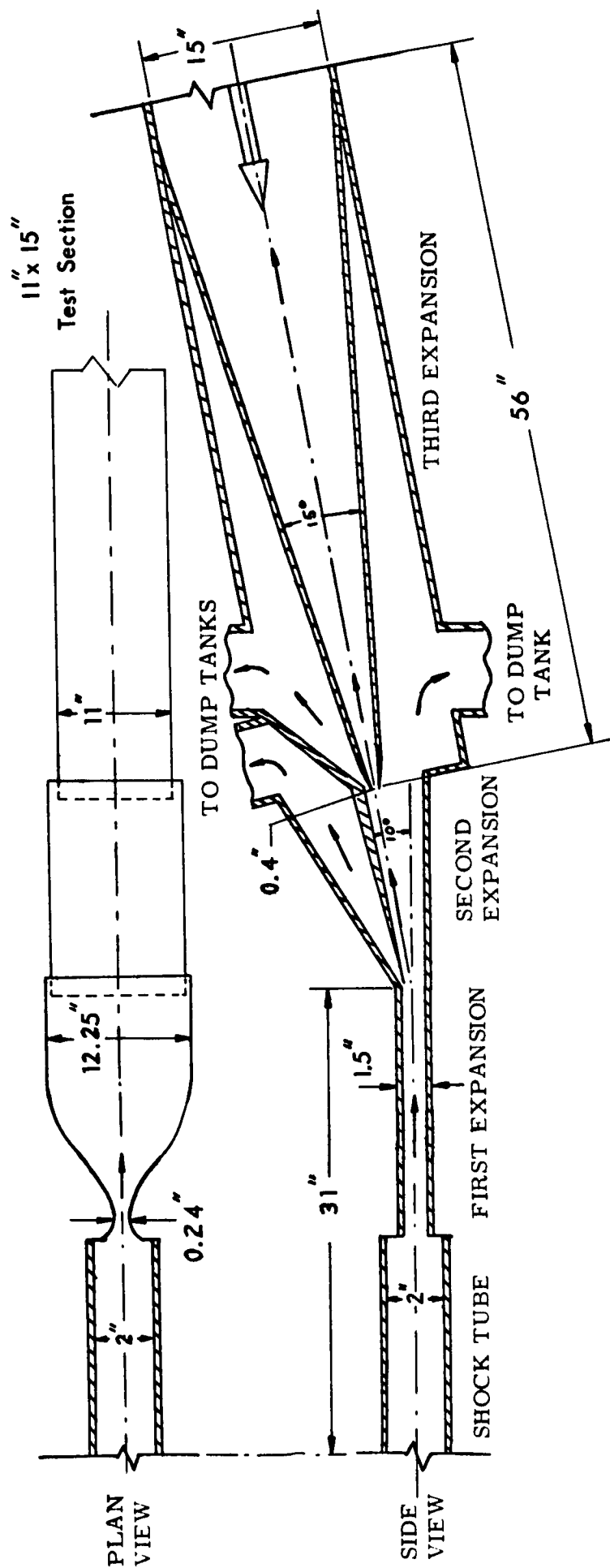
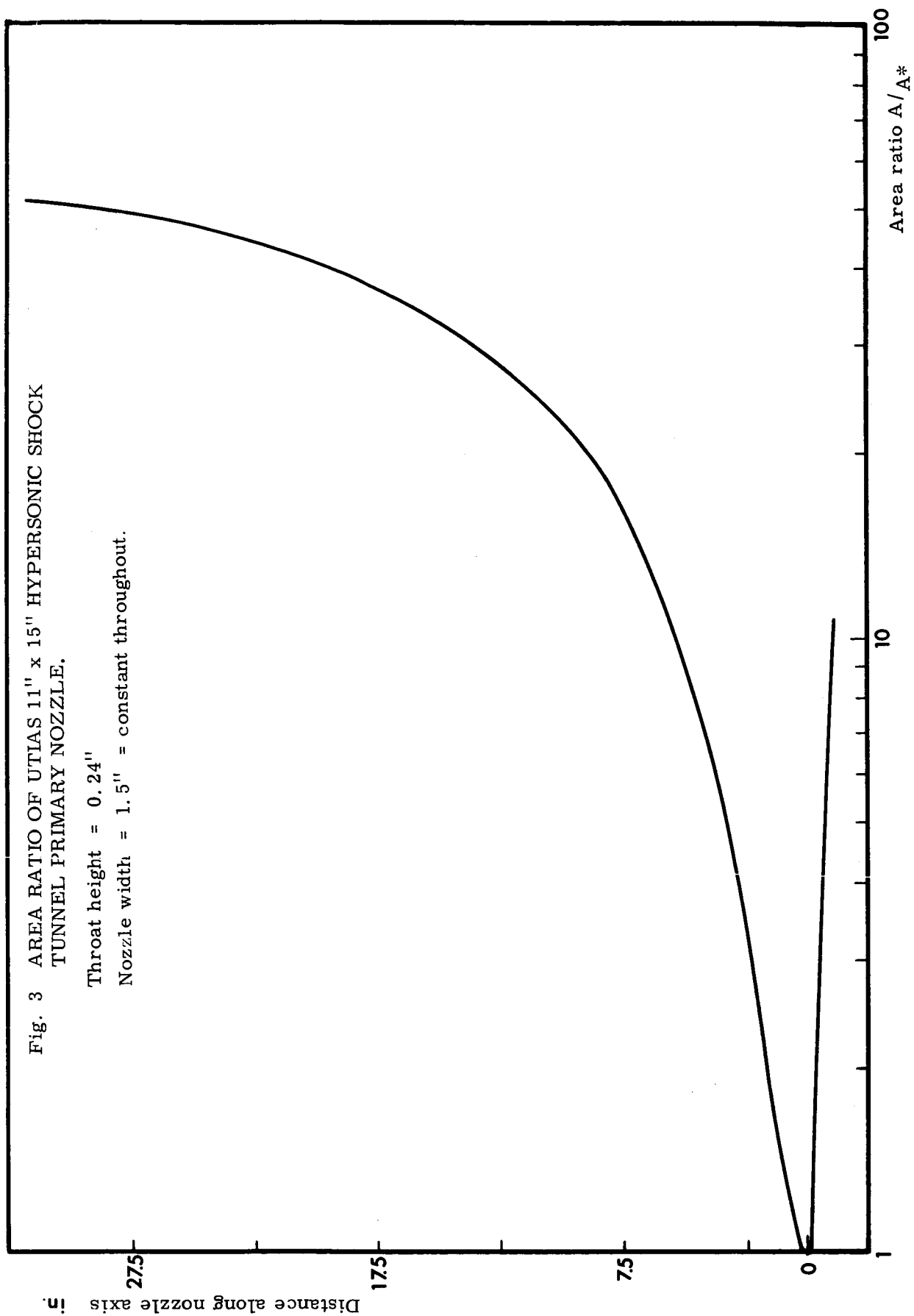


FIG. 2 AERODYNAMIC OUTLINE OF PRIMARY NOZZLE, CORNER EXPANSION PLATE, AND FINAL NOZZLE OF THE UTIAS 11 in. x 15 in. HYPERSONIC SHOCK TUNNEL (This portion of the facility was formerly designed and used by Cornell Aeronautical Laboratory, Inc., Buffalo, N. Y.)



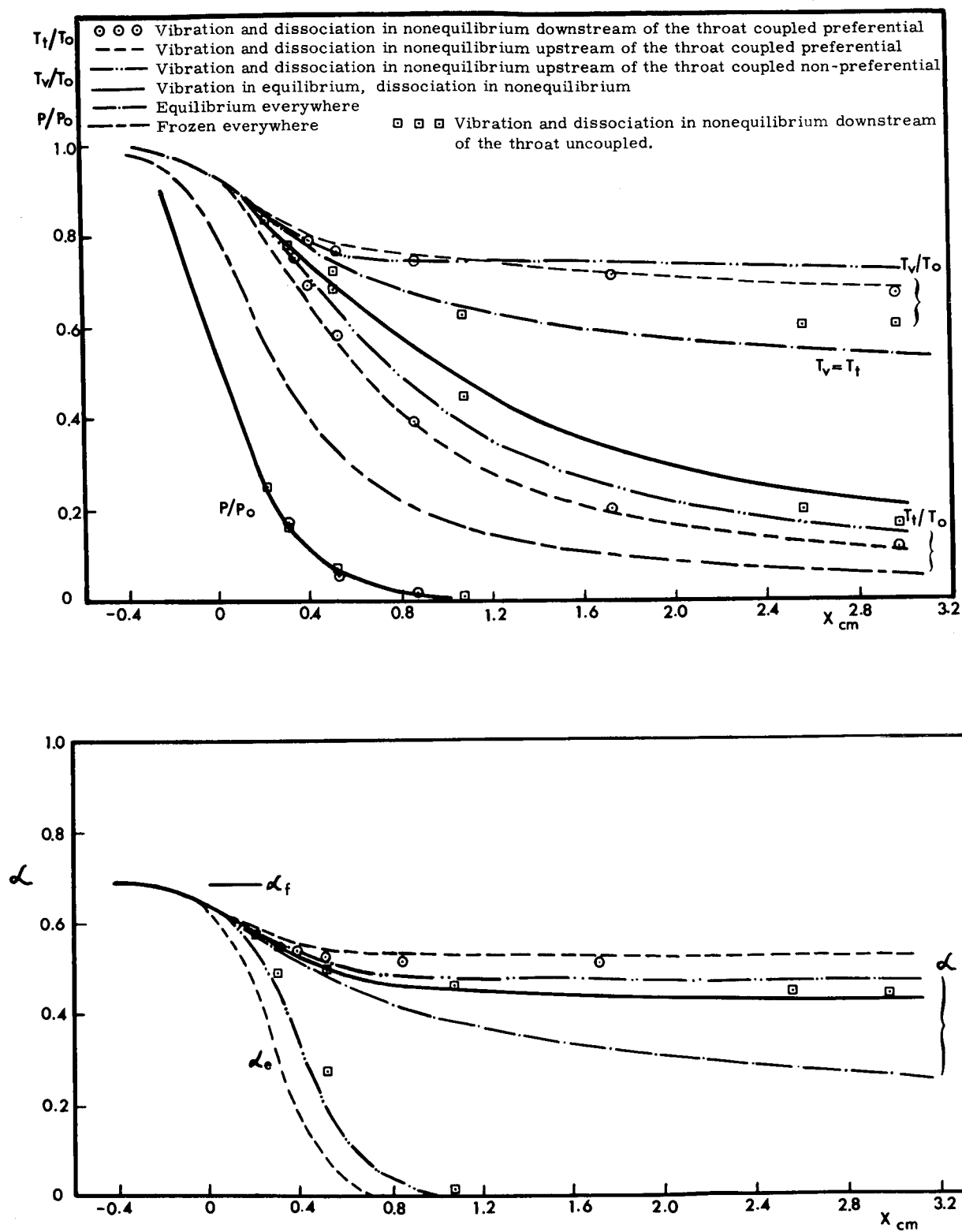


FIG. 4 DISTRIBUTION OF FLOW QUANTITIES IN A PRIMARY HYPERSONIC SHOCK TUNNEL NOZZLE USING VARIOUS VIBRATION-DISSOCIATION NONEQUILIBRIUM
 $P_o = 82 \text{ atm}$, $T_o = 5900^\circ\text{K}$ $\alpha_o = 0.69$

Fig. 4C COMPARISON BETWEEN DERIVATIVES $\frac{dT_t}{dx}$, $\frac{dT_r}{dx}$, $\frac{d\alpha}{dx}$ STARTING NONEQUILIBRIUM CALCULATIONS AT DIFFERENT POINTS IN THE NOZZLE.

Axisymmetric hyperbolic nozzle-coupled preferential dissociation model

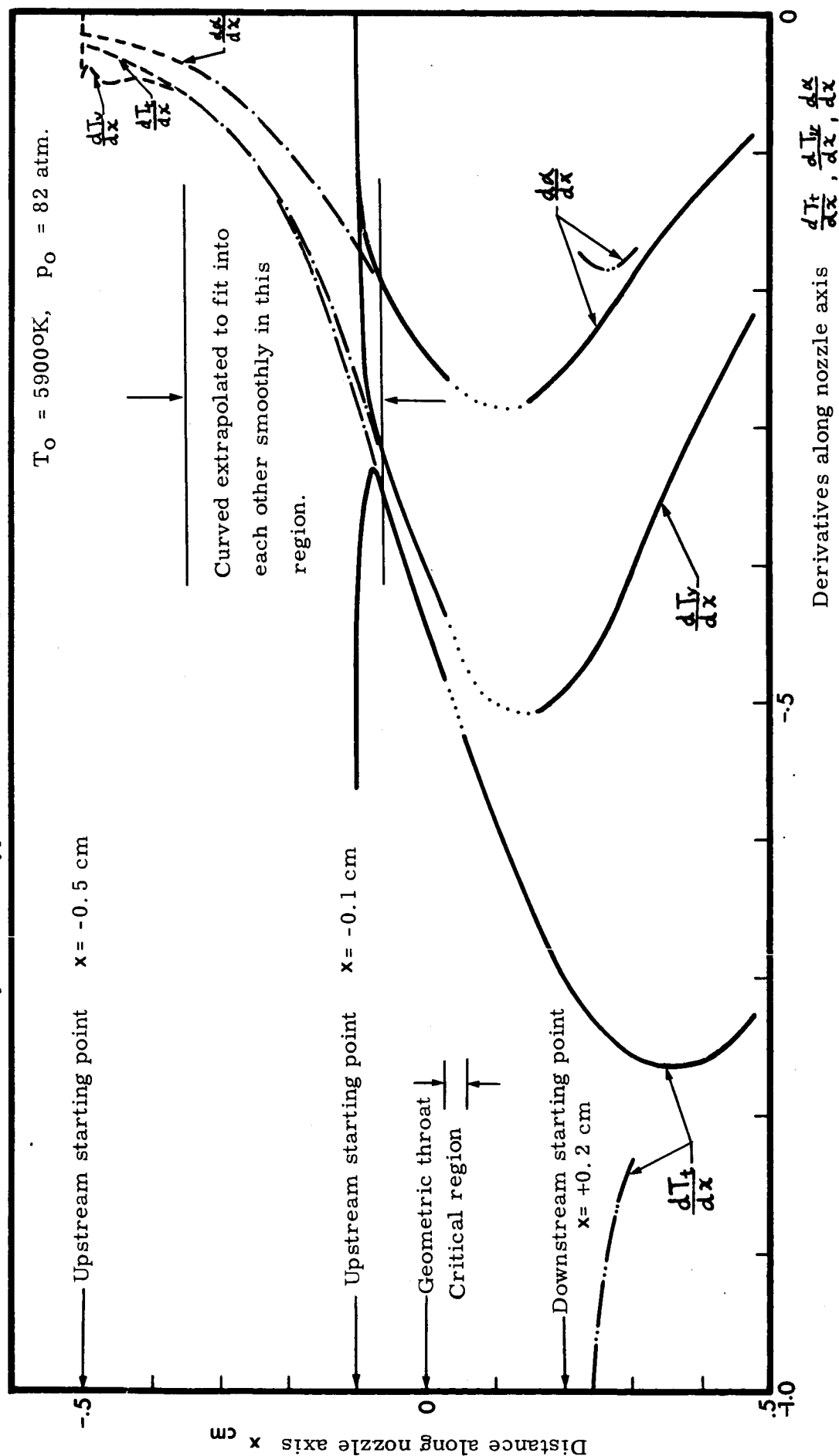
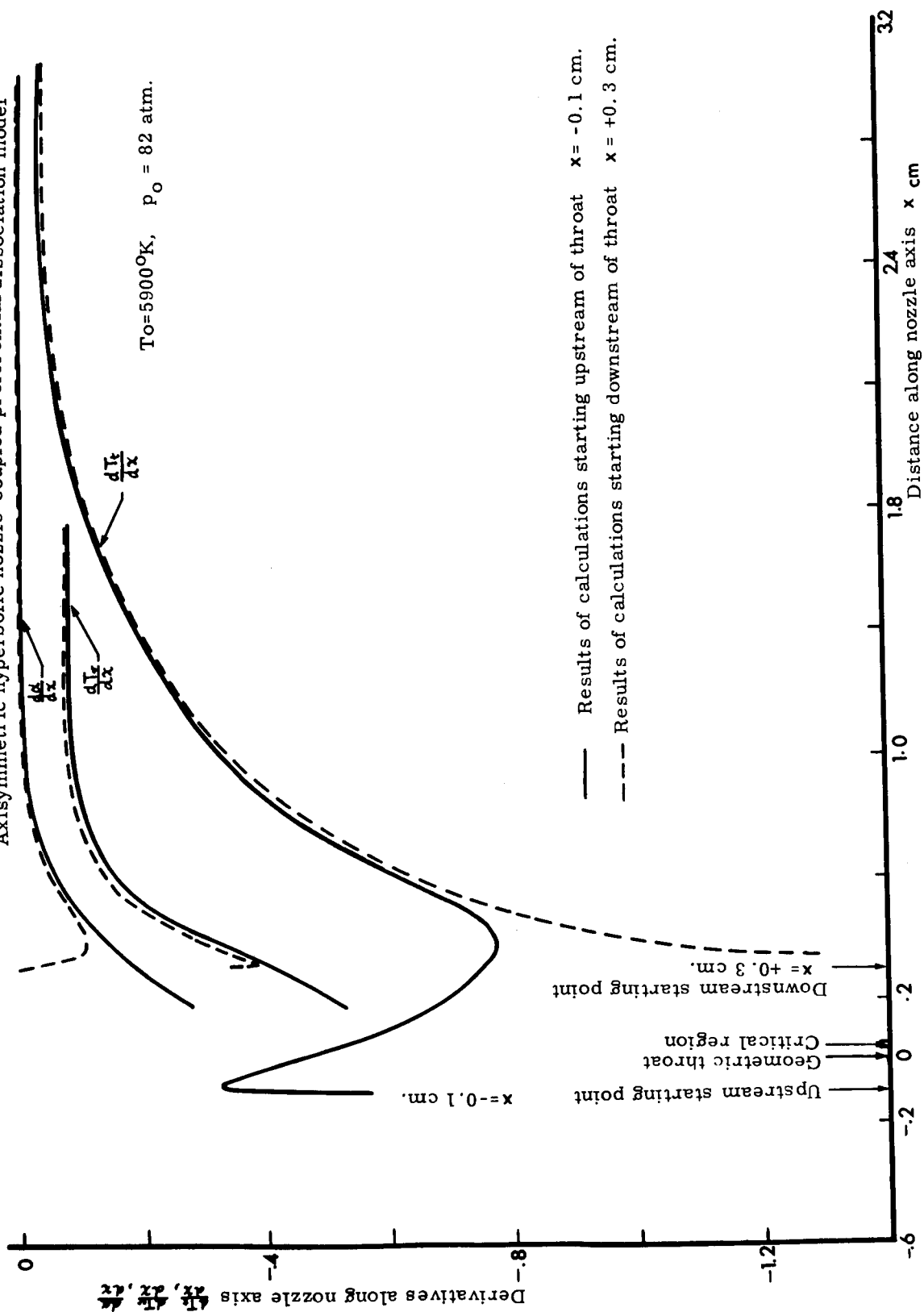


Fig. 4d

COMPARISON BETWEEN DERIVATIVES $\frac{dT}{dx}$, $\frac{dI}{dx}$, $\frac{dL}{dx}$
STARTING NONEQUILIBRIUM CALCULATIONS UPSTREAM

DOWNSTREAM OF THROAT.

Axisymmetric hyperbolic nozzle-coupled preferential dissociation model



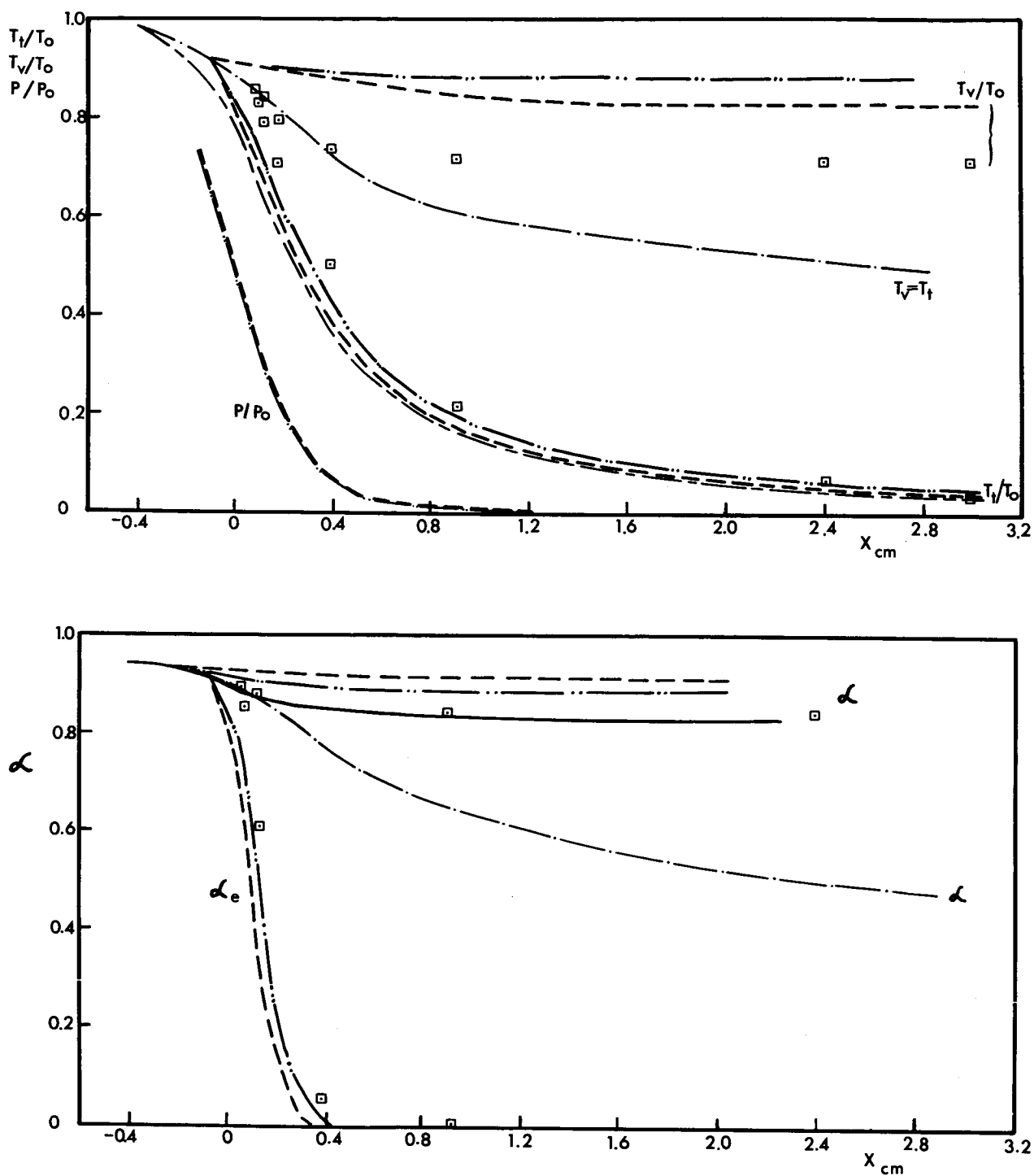
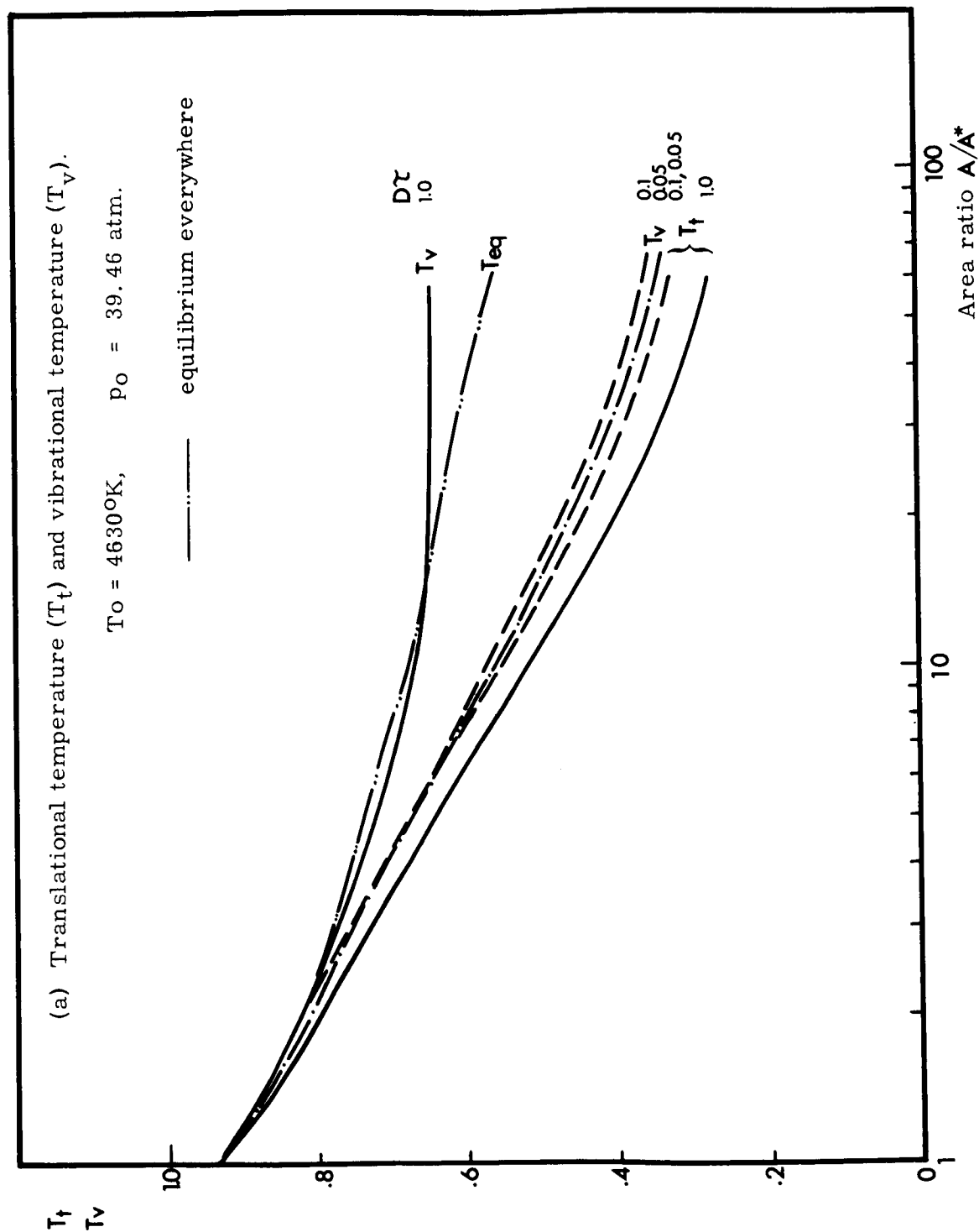


FIG. 5 DISTRIBUTION OF FLOW QUANTITIES IN A PRIMARY HYPERSONIC SHOCK TUNNEL NOZZLE USING VARIOUS VIBRATION-DISSOCIATION NONEQUILIBRIUM COUPLING MODELS

$p_0 = 9.4 \text{ atm}$, $T_0 = 5900^\circ\text{K}$, $\alpha_0 = 0.96$

- ⊙ ⊙ ⊙ Vibration and dissociation in nonequilibrium downstream of the throat coupled preferential
- Vibration and dissociation in nonequilibrium upstream of the throat coupled preferential
- Vibration and dissociation in nonequilibrium upstream of the throat coupled non-preferential
- Vibration in equilibrium, dissociation in nonequilibrium
- Equilibrium everywhere
- Frozen everywhere
- □ □ Vibration and dissociation in nonequilibrium downstream of the throat uncoupled

Fig. 6 VARIATION OF FLOW QUANTITIES ALONG THE NOZZLE AXIS
UTIAS 11" x 15" Hypersonic Shock Tunnel Primary Nozzle.



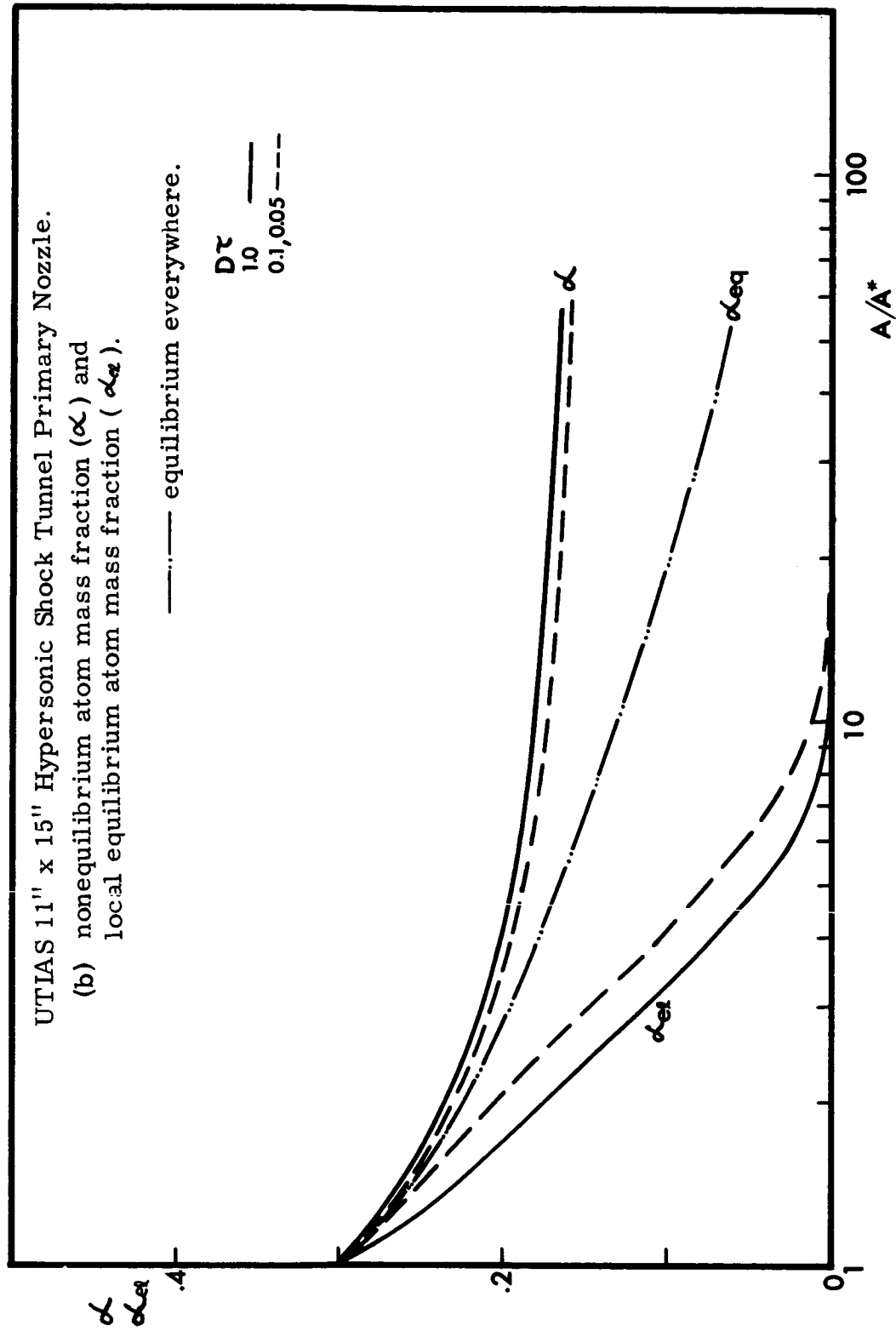


FIG. 6 (continued)

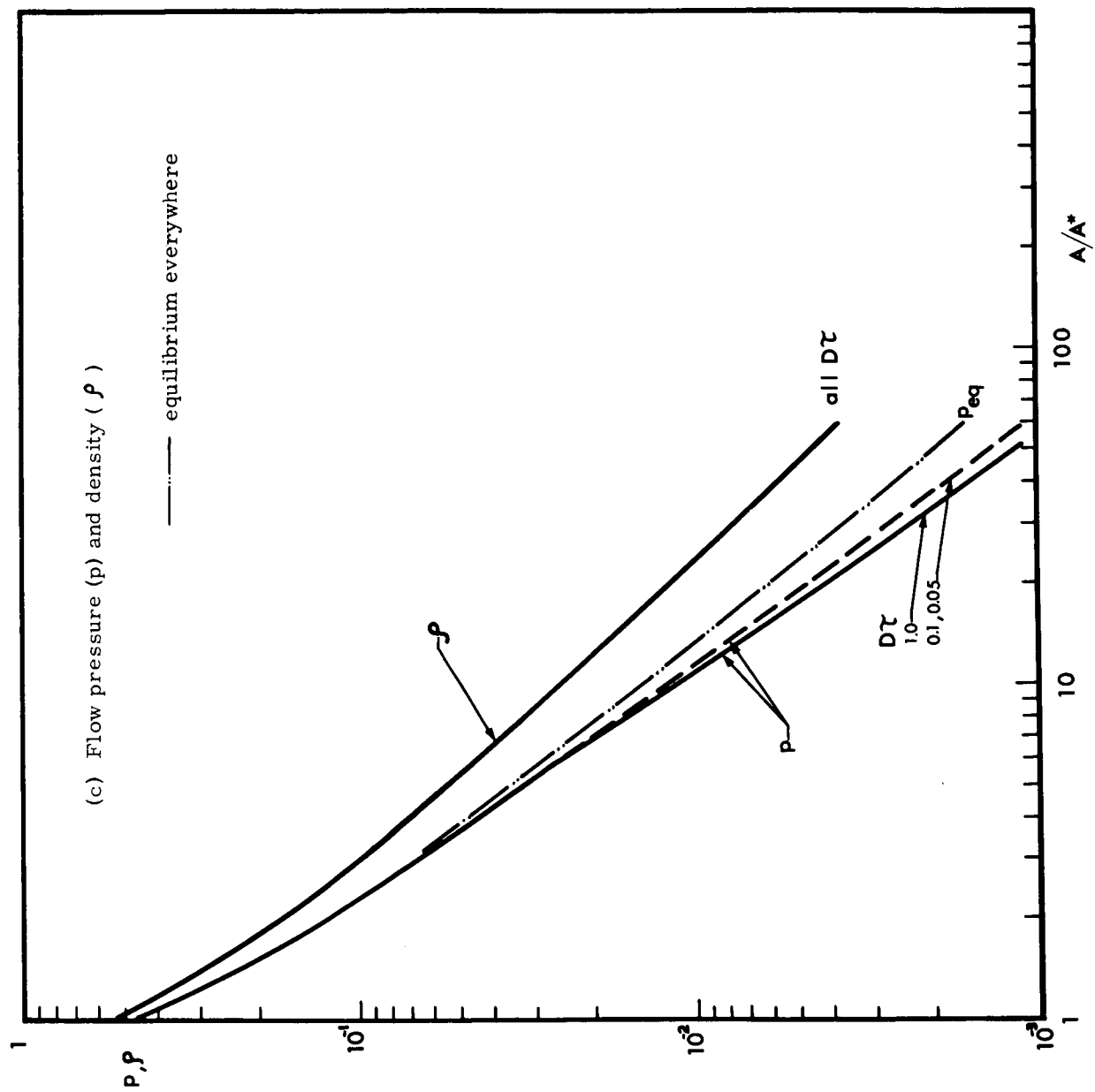


FIG. 6 (continued)

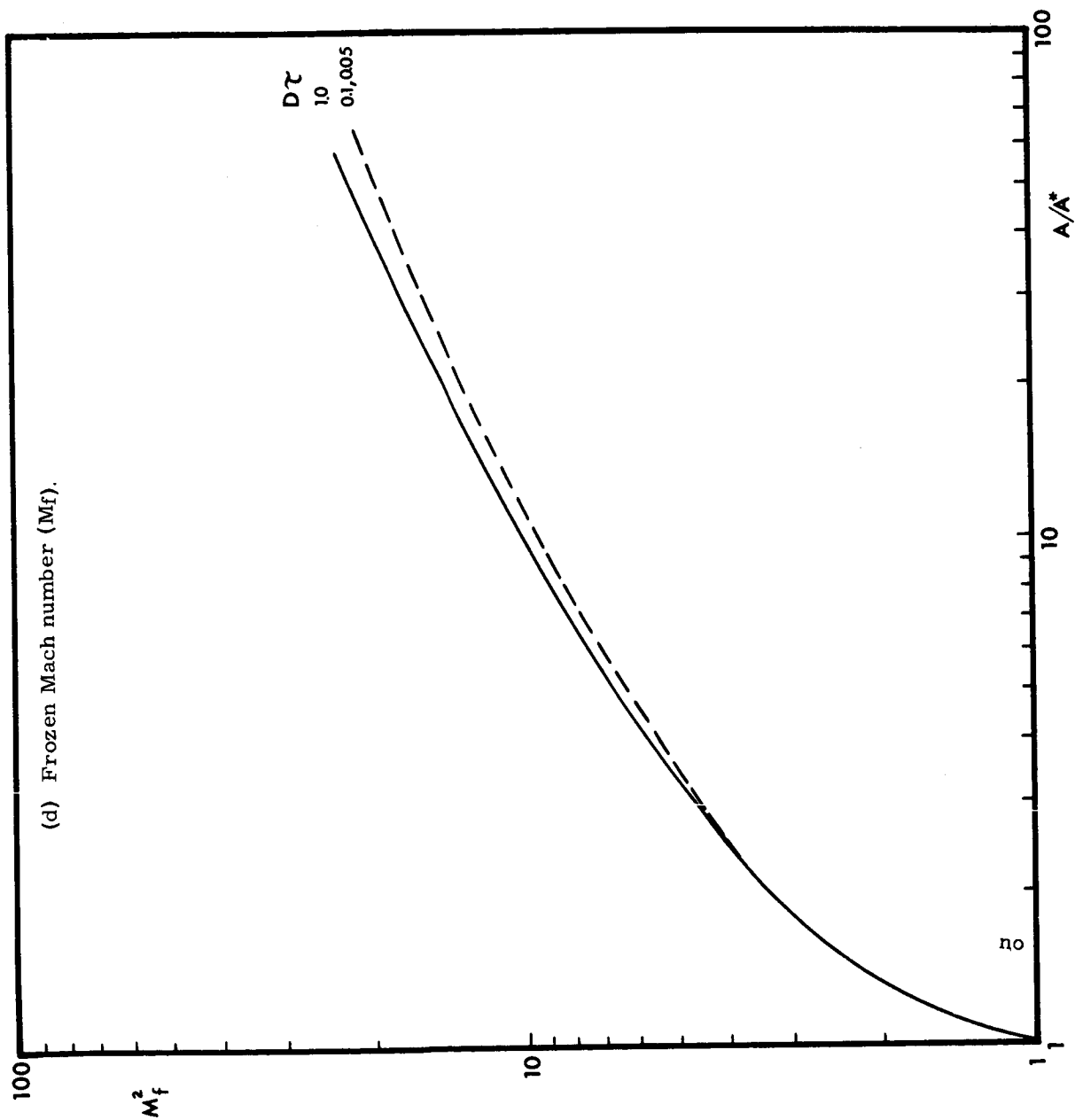


FIG. 6 (continued)

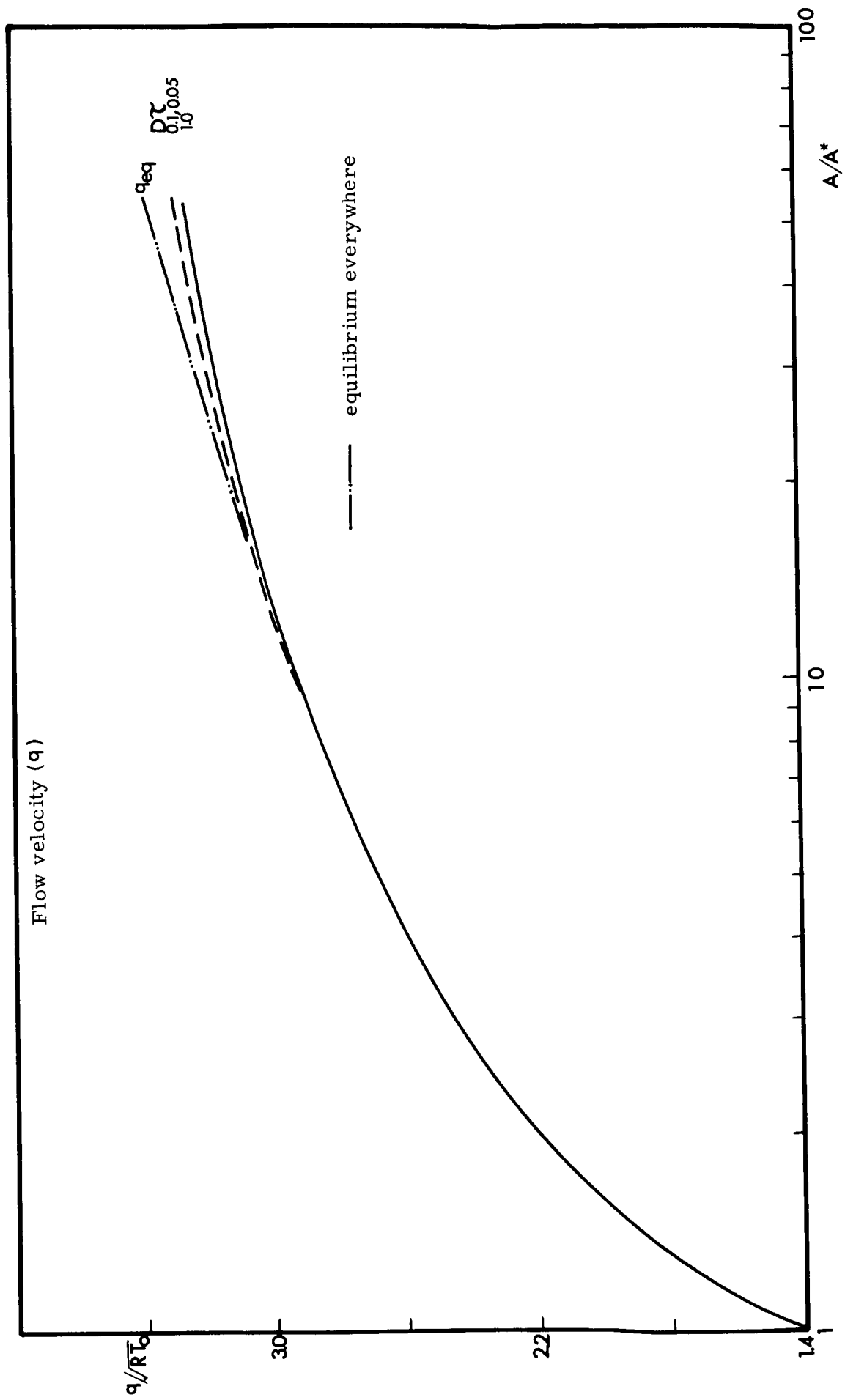


FIG. 6 (continued)

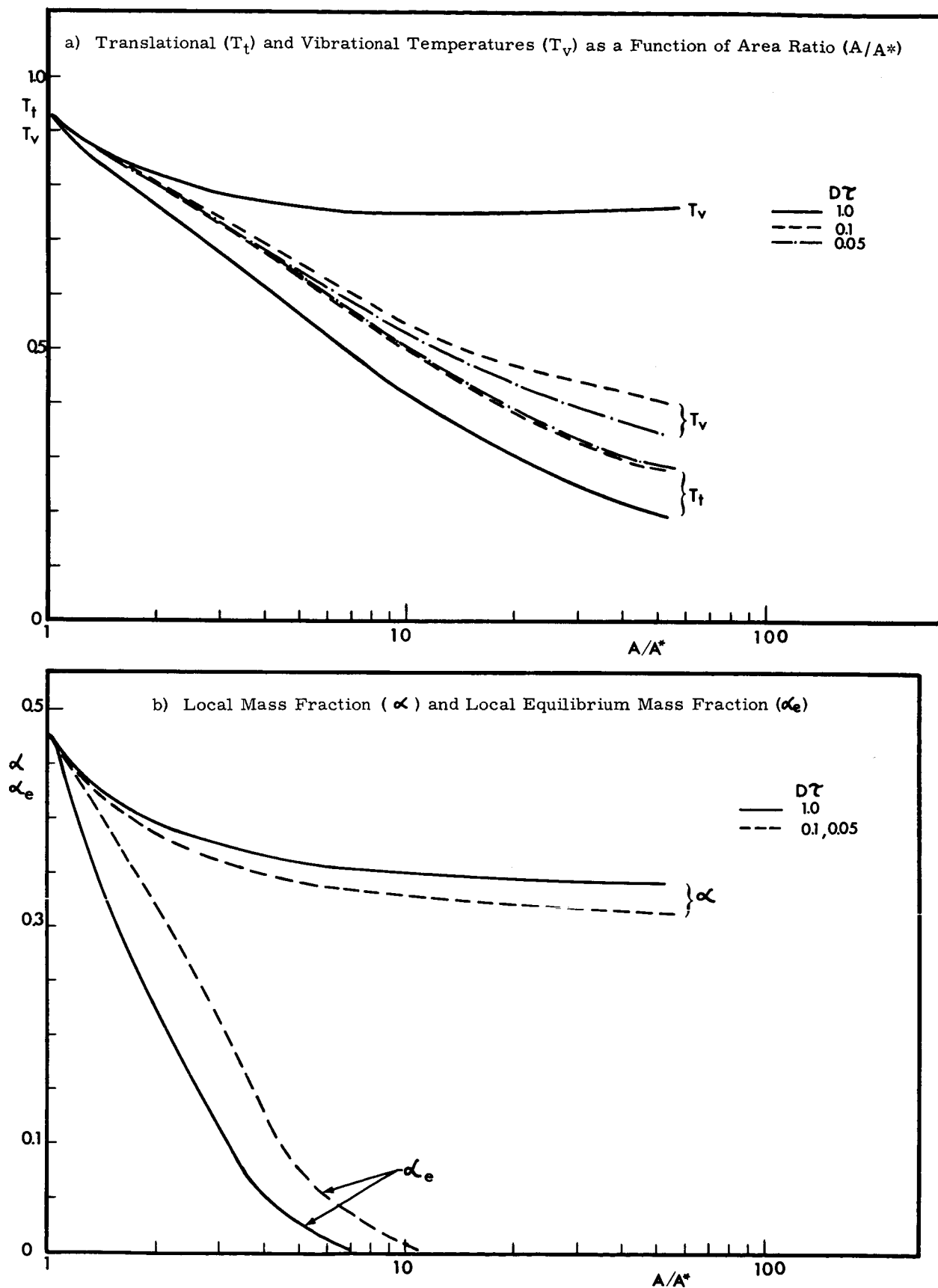


FIG. 7 DISTRIBUTION OF FLOW QUANTITIES IN THE UTIAS 11 in. x 15 in. HYPERSONIC SHOCK TUNNEL PRIMARY NOZZLE USING VARIOUS VIBRATION-DISSOCIATION NONEQUILIBRIUM COUPLING MODELS

$p_o = 22.1 \text{ atm}$, $T_o = 4800^\circ\text{K}$, $\alpha_o = 0.52$

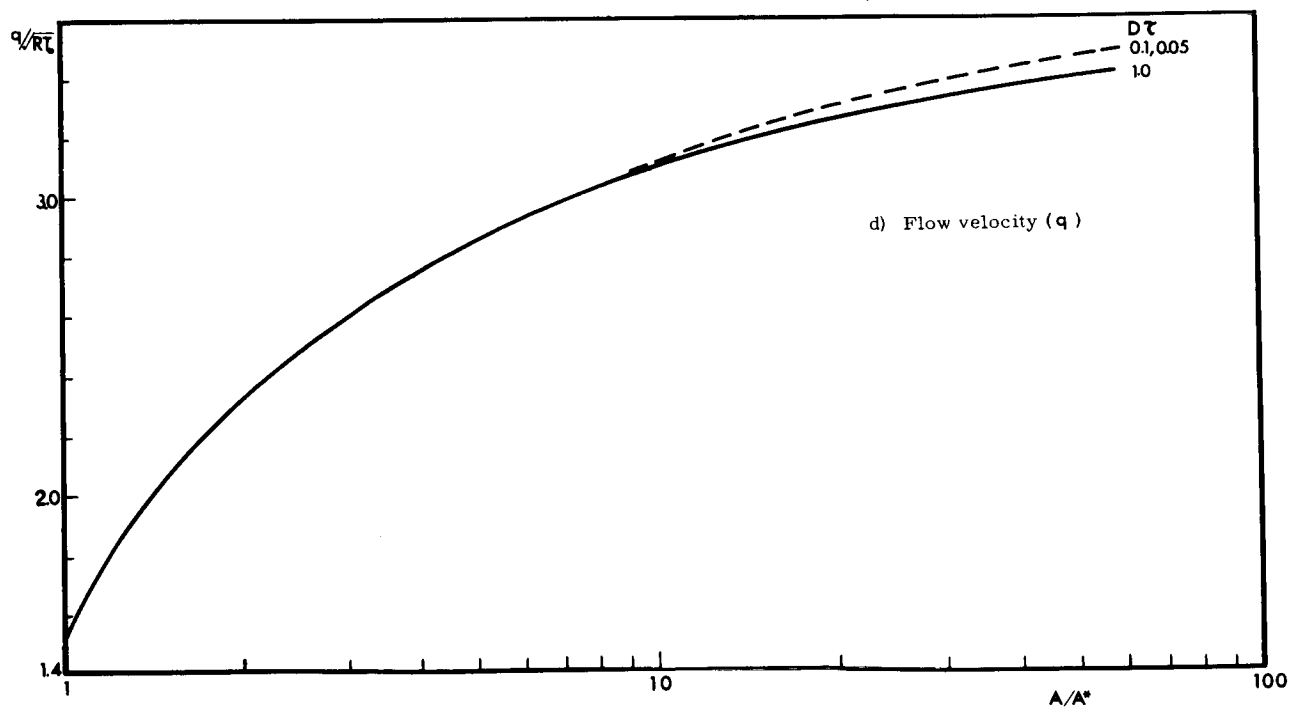
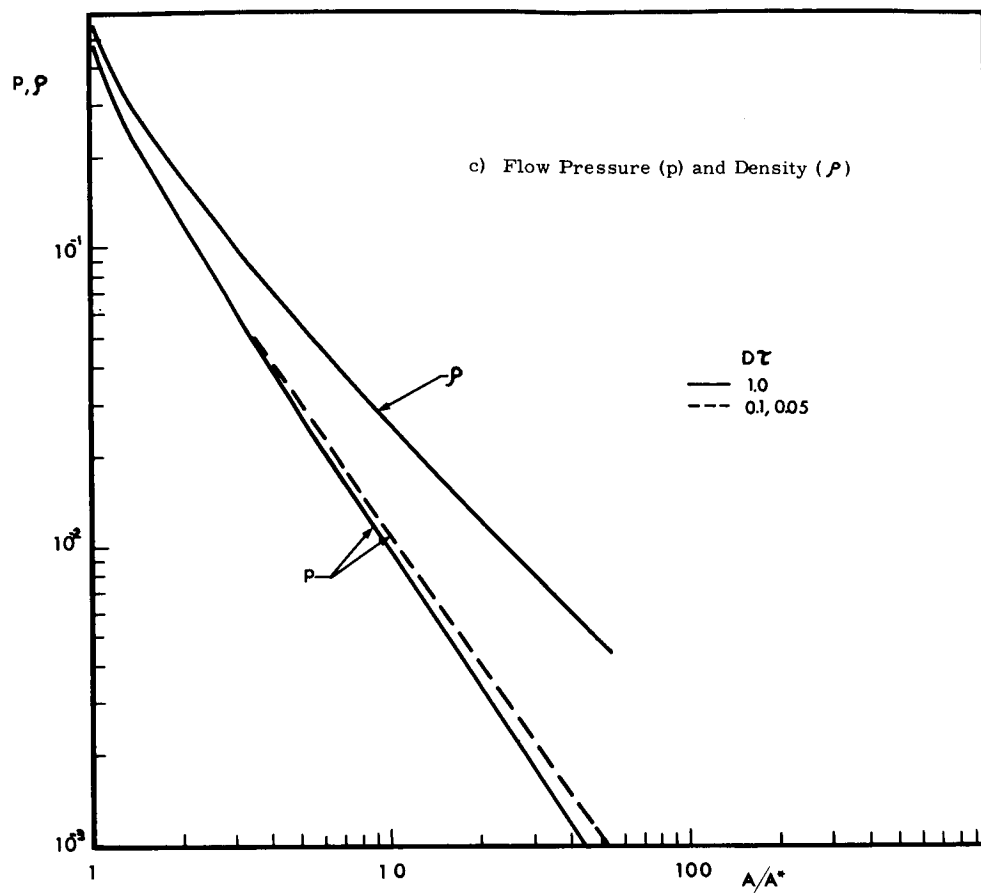


FIG. 7 (continued)

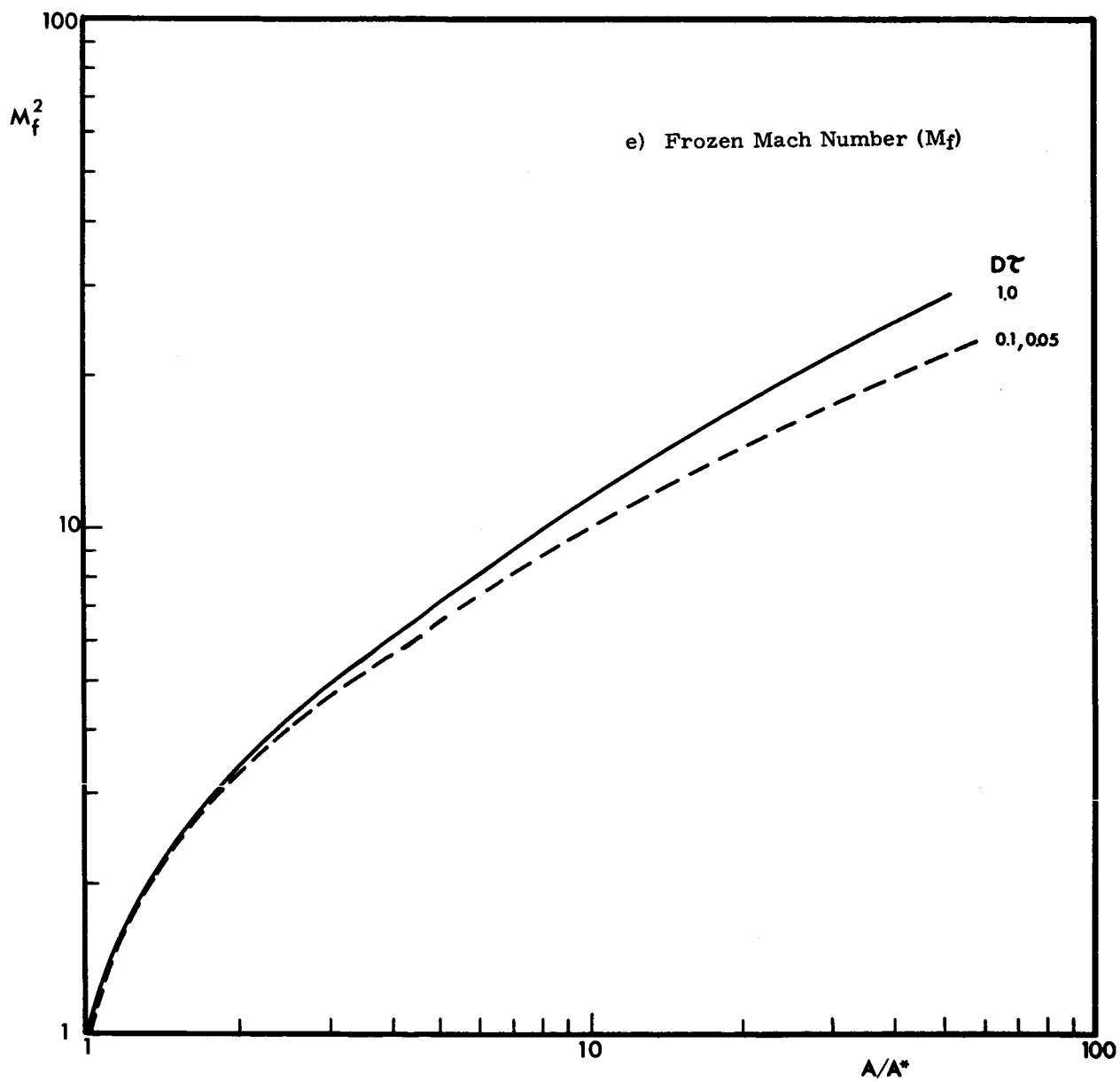
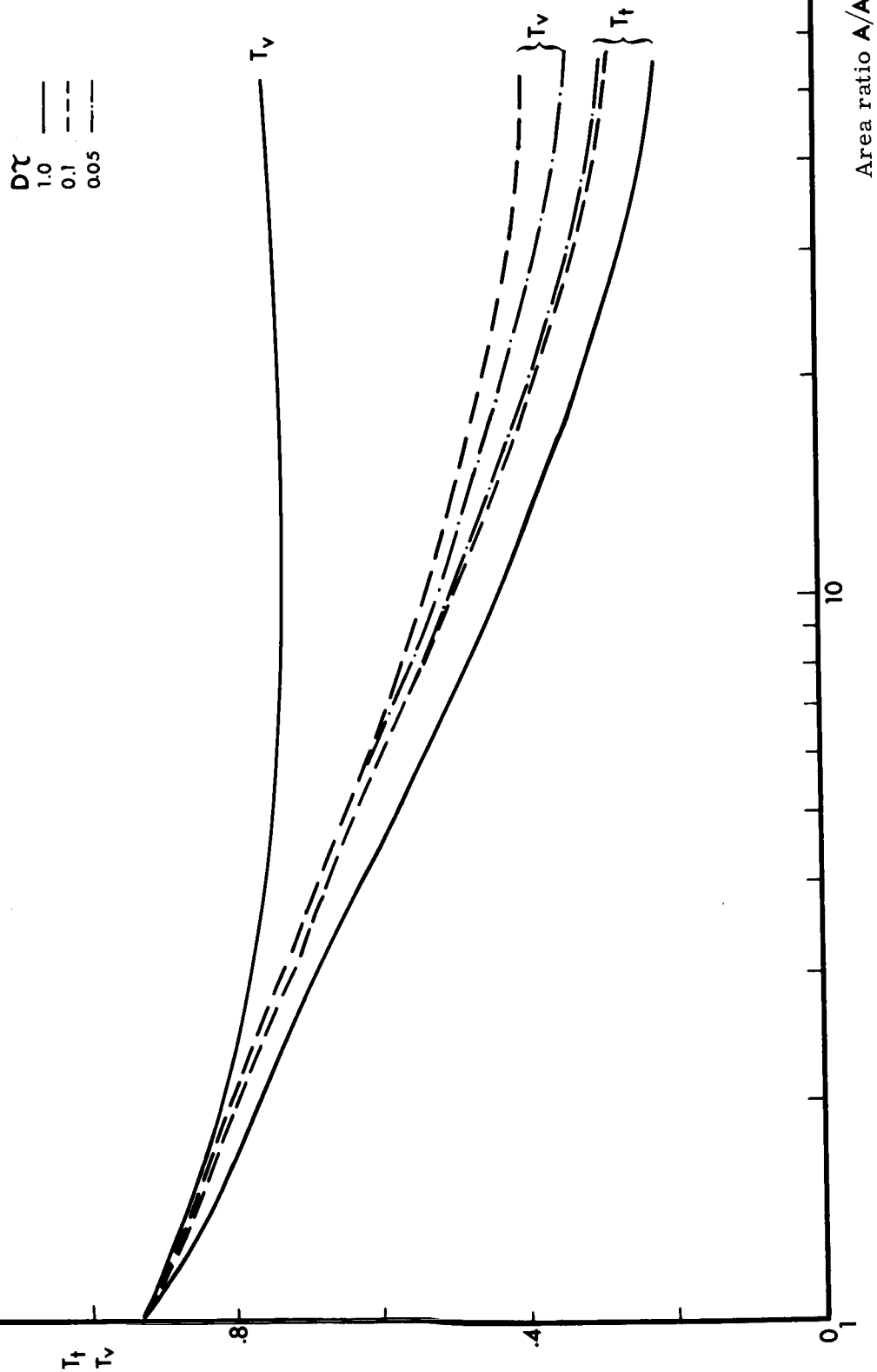


FIG. 7 (concluded)

Fig. 8 VARIATION OF FLOW QUANTITIES ALONG THE NOZZLE AXIS
 UTIAS 11" x 15" Hypersonic Shock Tunnel Primary Nozzle.
 $T_0 = 4600^\circ\text{K}$, $p_0 = 22.45 \text{ atm}$.

(a) Translational temperature (T_t) and vibrational temperature (T_v)



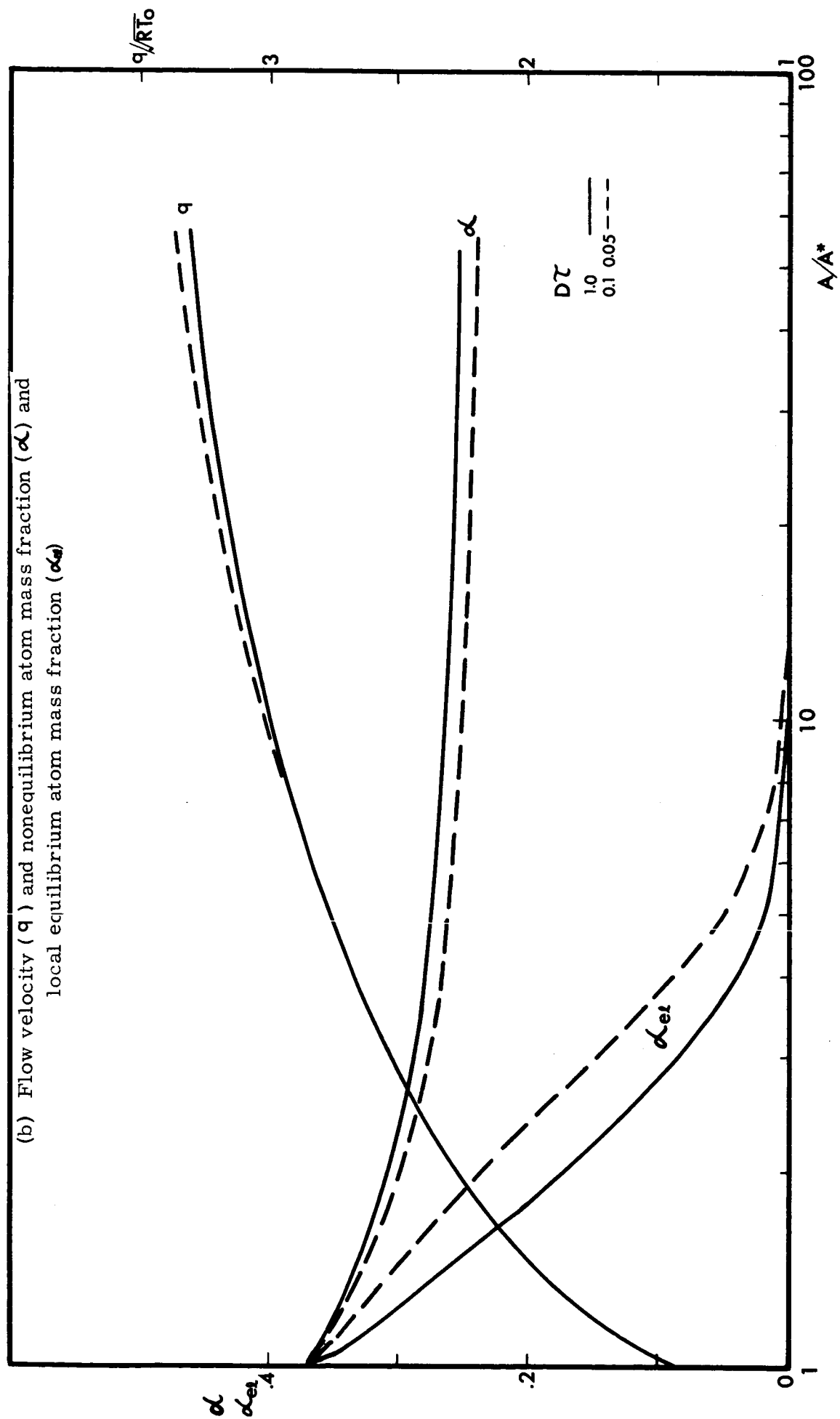


FIG. 8 (continued)

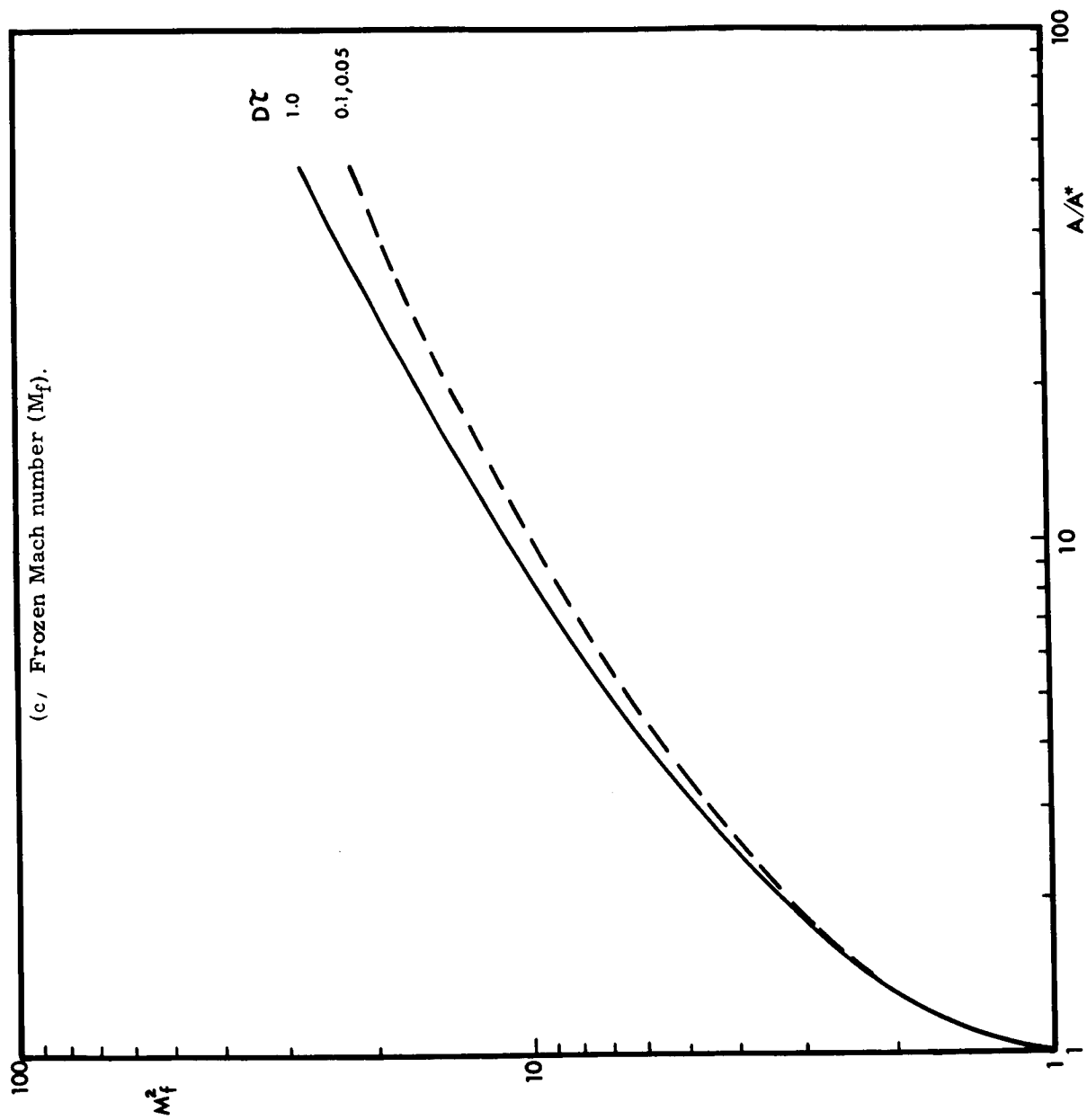


FIG. 8 (continued)

Fig. 9 VARIATION OF FLOW QUANTITIES ALONG THE NOZZLE AXIS

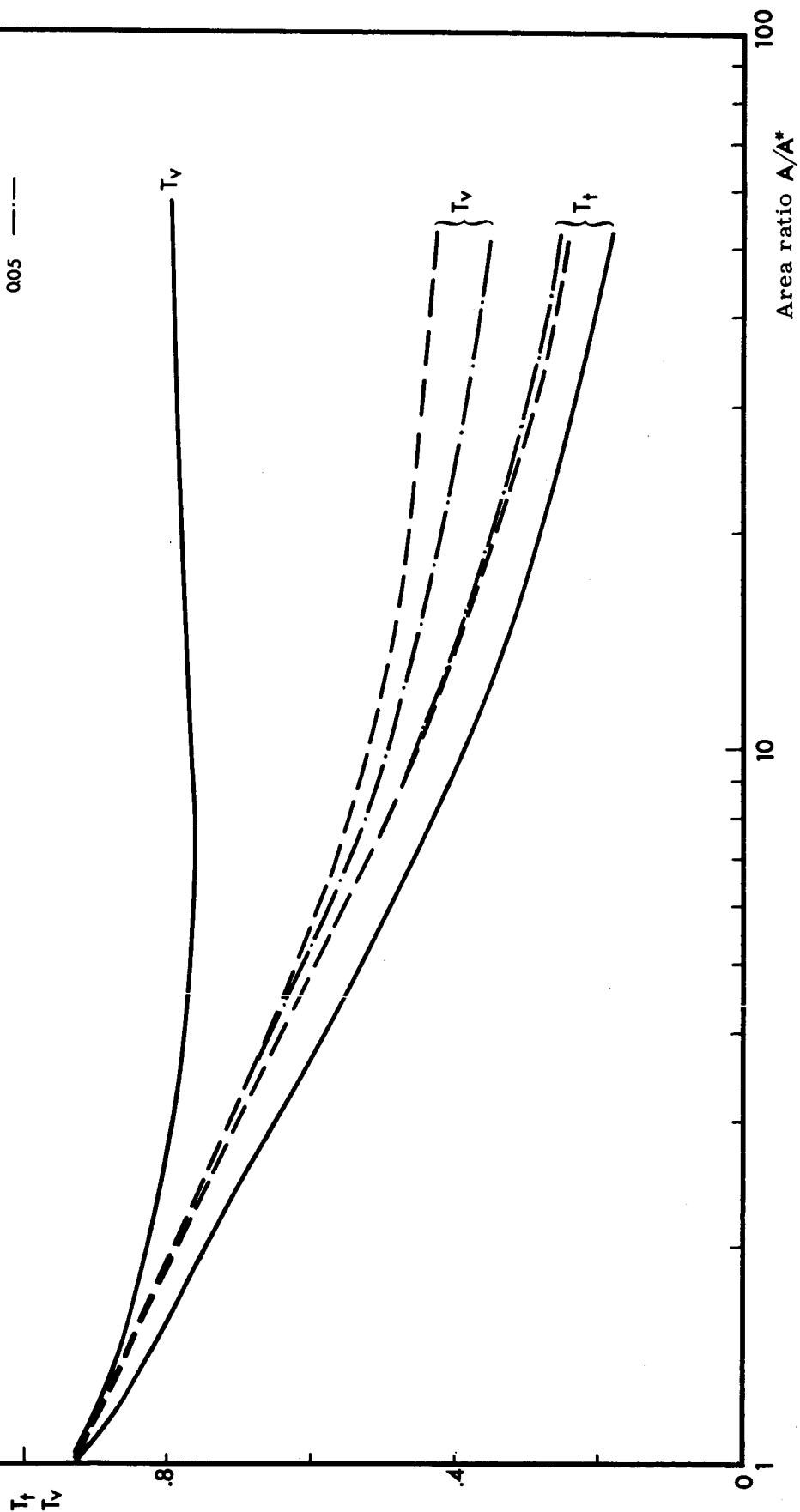
UTIAS 11" x 15" Hypersonic Shock Tunnel Primary Nozzle.

$T_o = 4350^{\circ}\text{K}$, $p_o = 14.18 \text{ atm}$.

(a) Translational temperature (T_t) and vibrational temperature (T_v).

$D\tau$

—	1.0
- - -	0.1
- · - · -	0.05



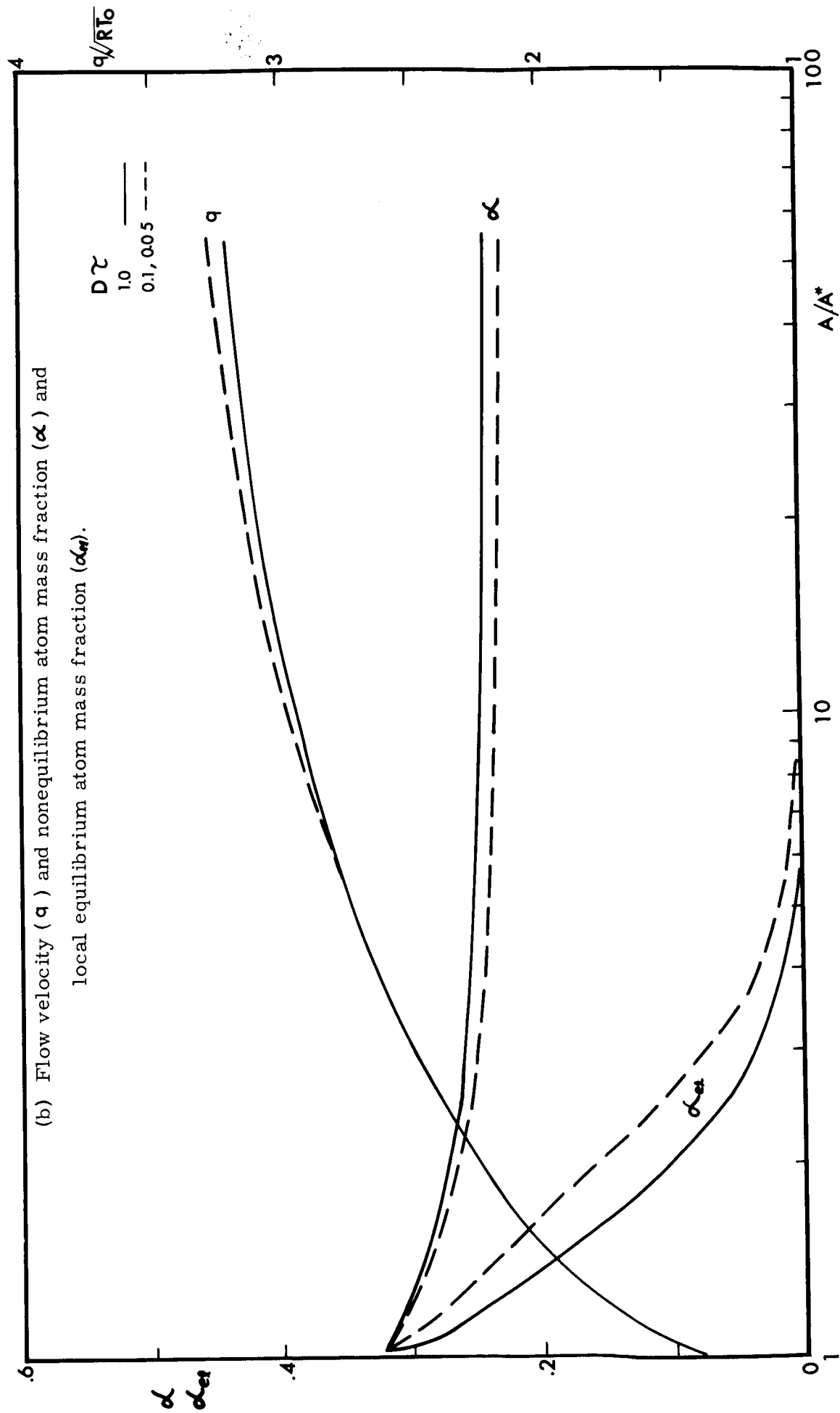


FIG. 9 (continued)

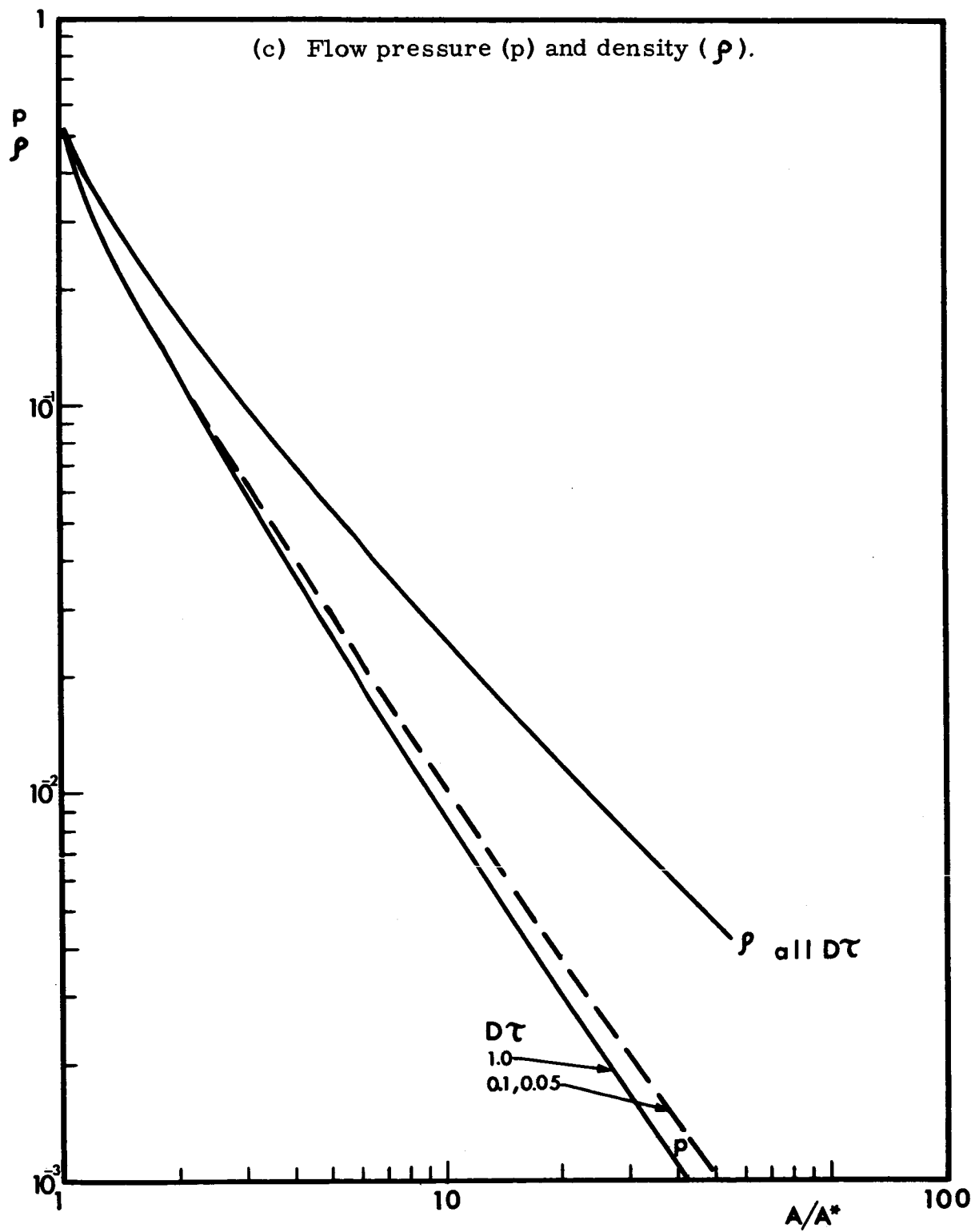


FIG. 9 (continued)

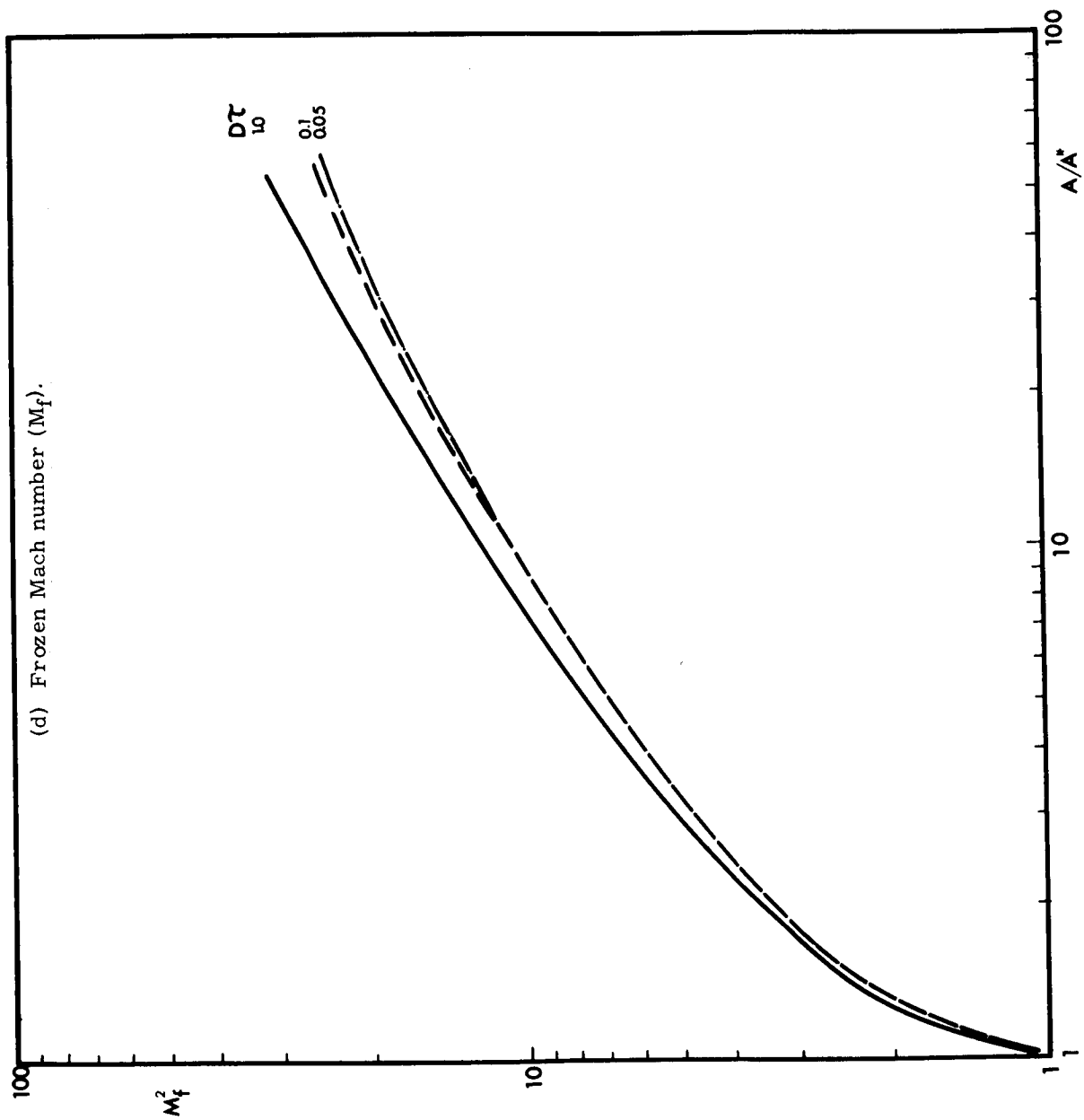
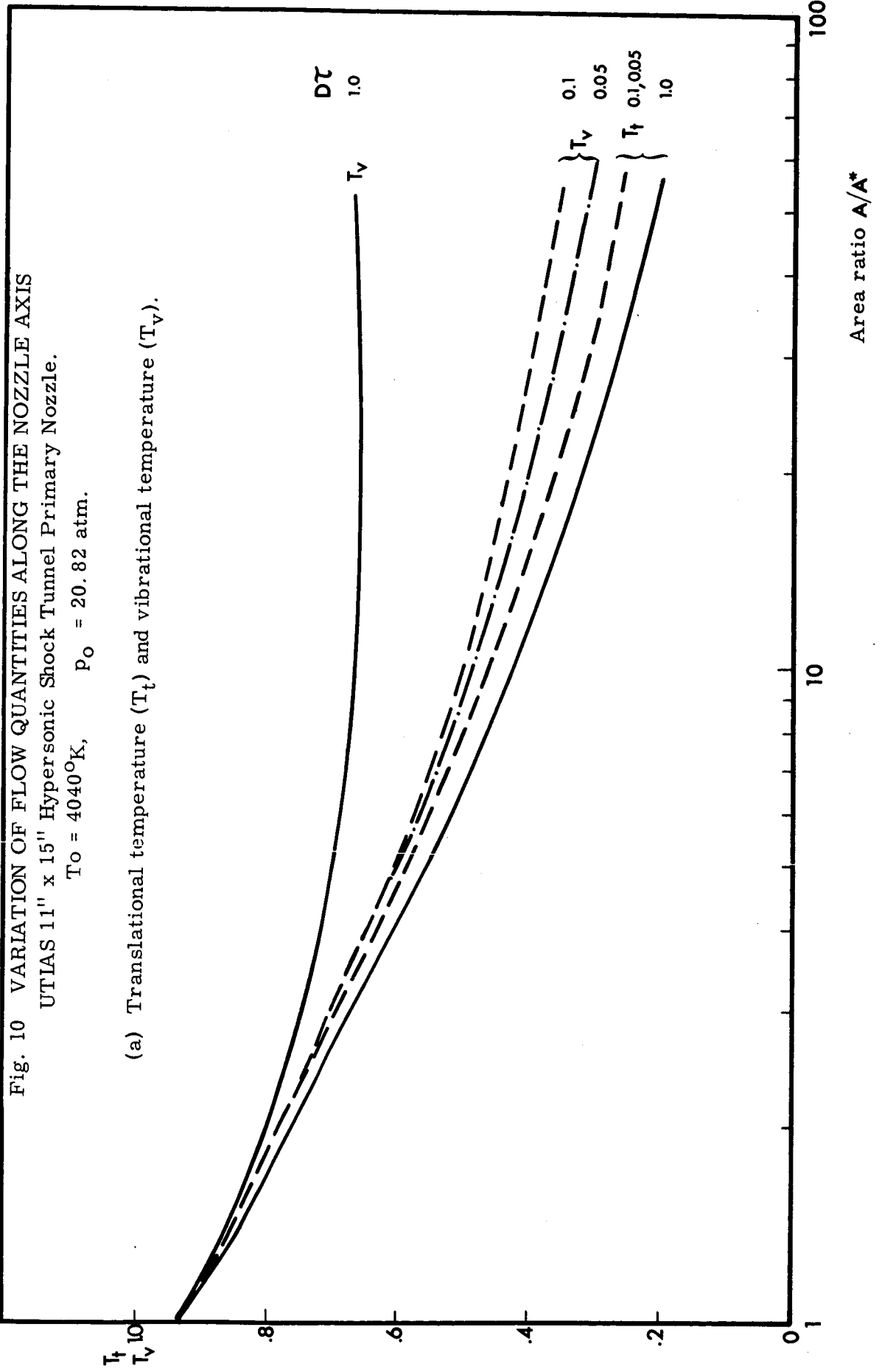


FIG. 9 (continued)



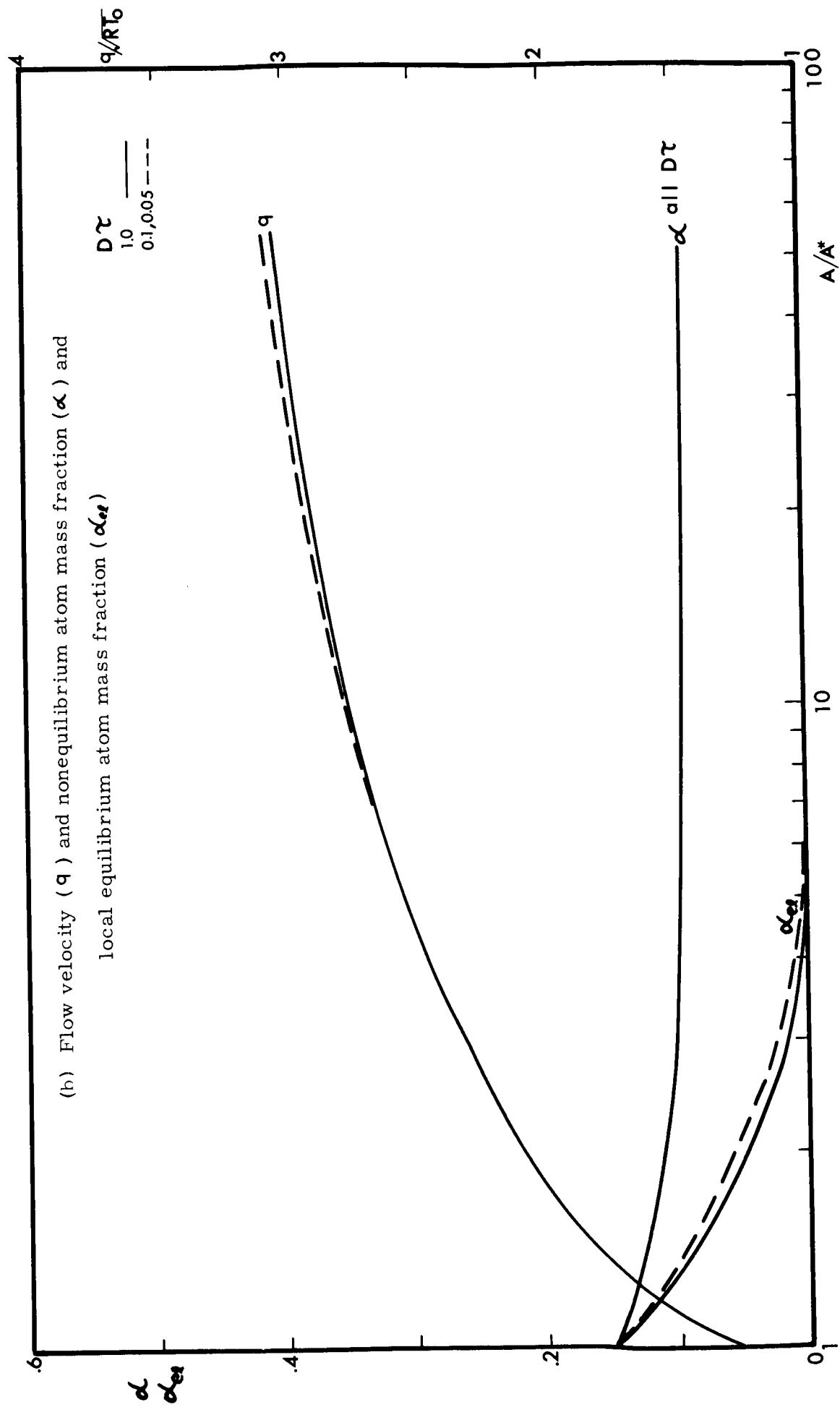


FIG. 10 (continued)

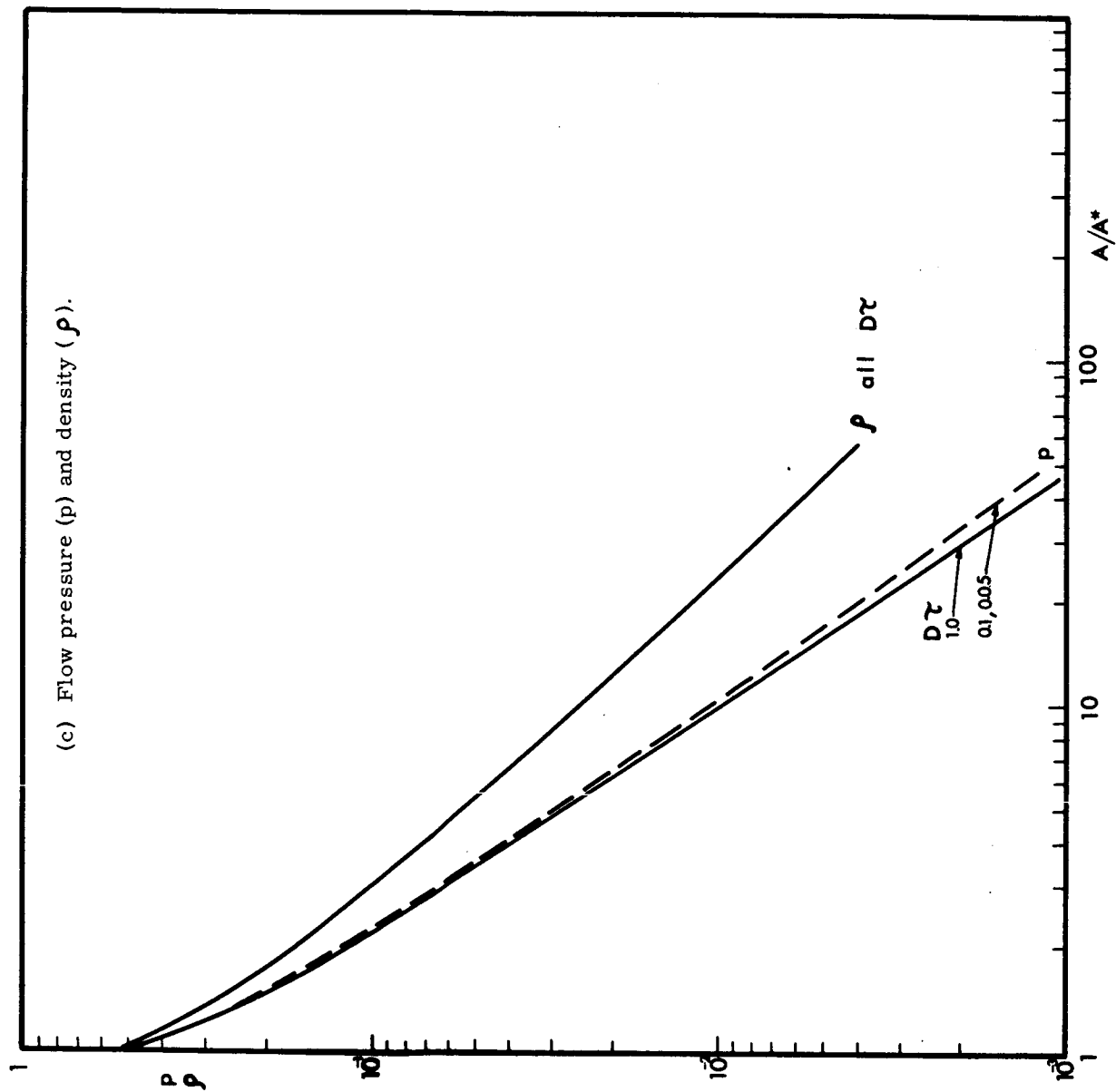


FIG. 10 (continued)

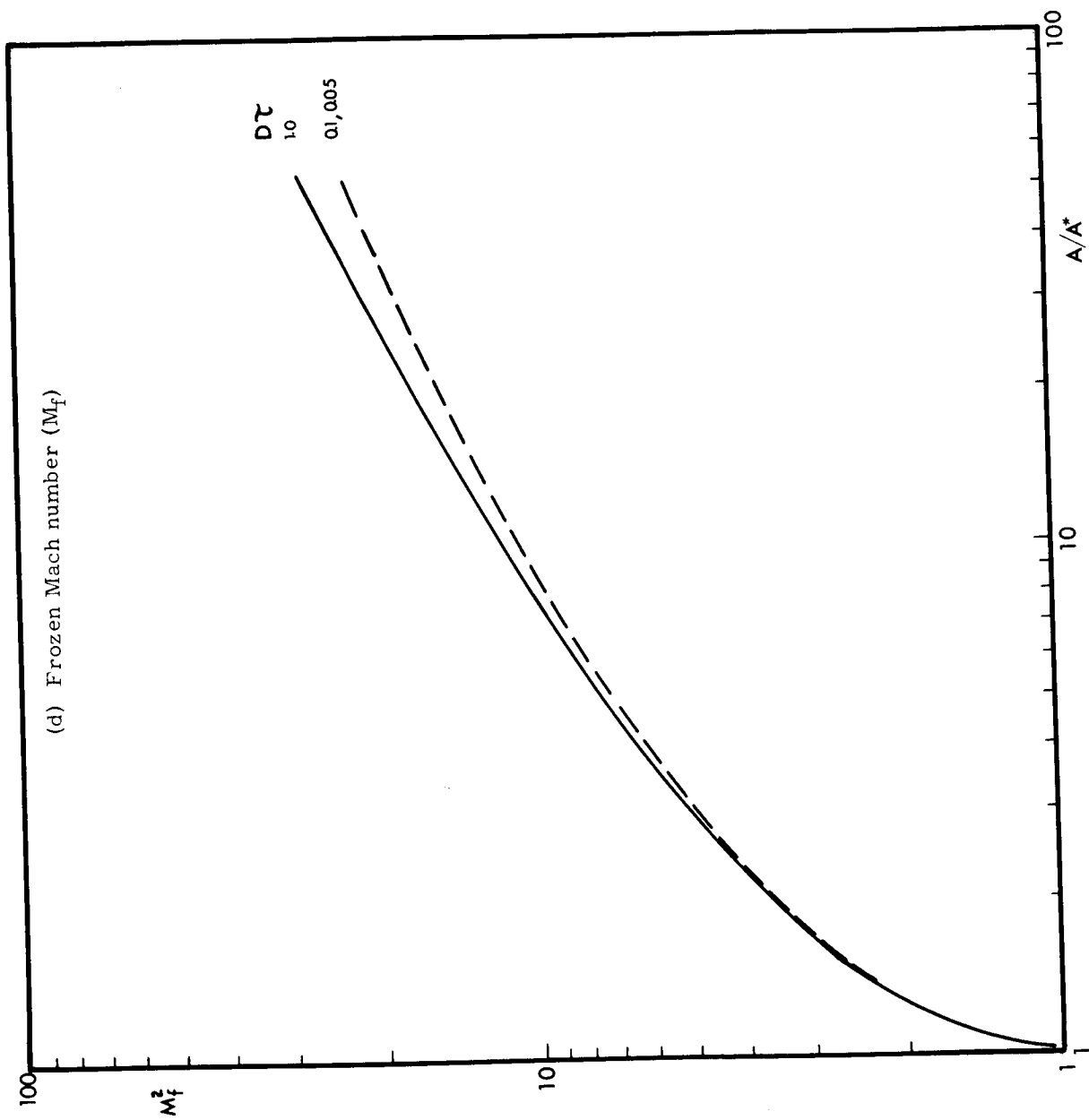
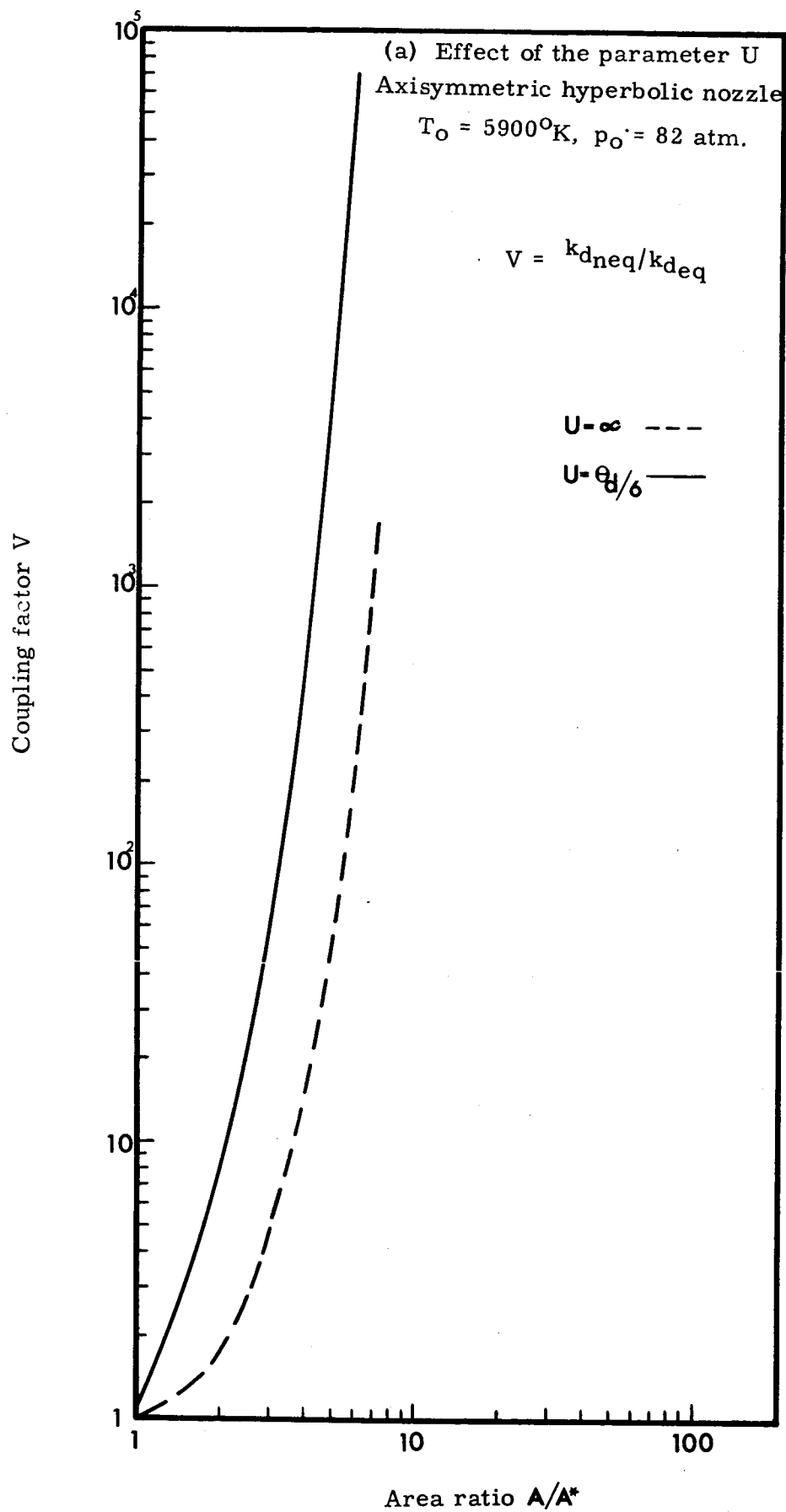


FIG. 10 (continued)

Fig. 11 VARIATION OF COUPLING FACTOR V ALONG THE NOZZLE AXIS.



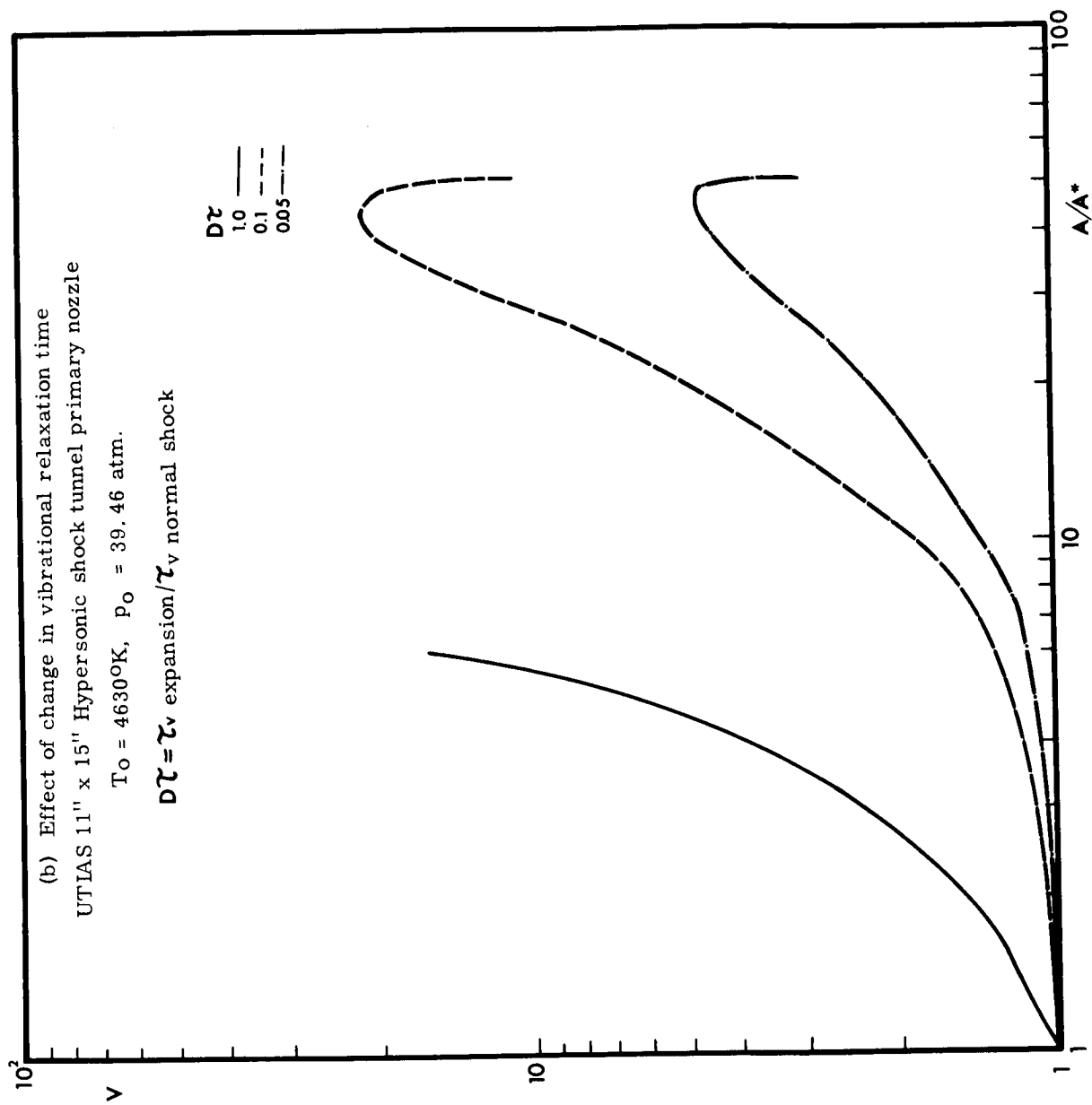


FIG. 11 (continued)

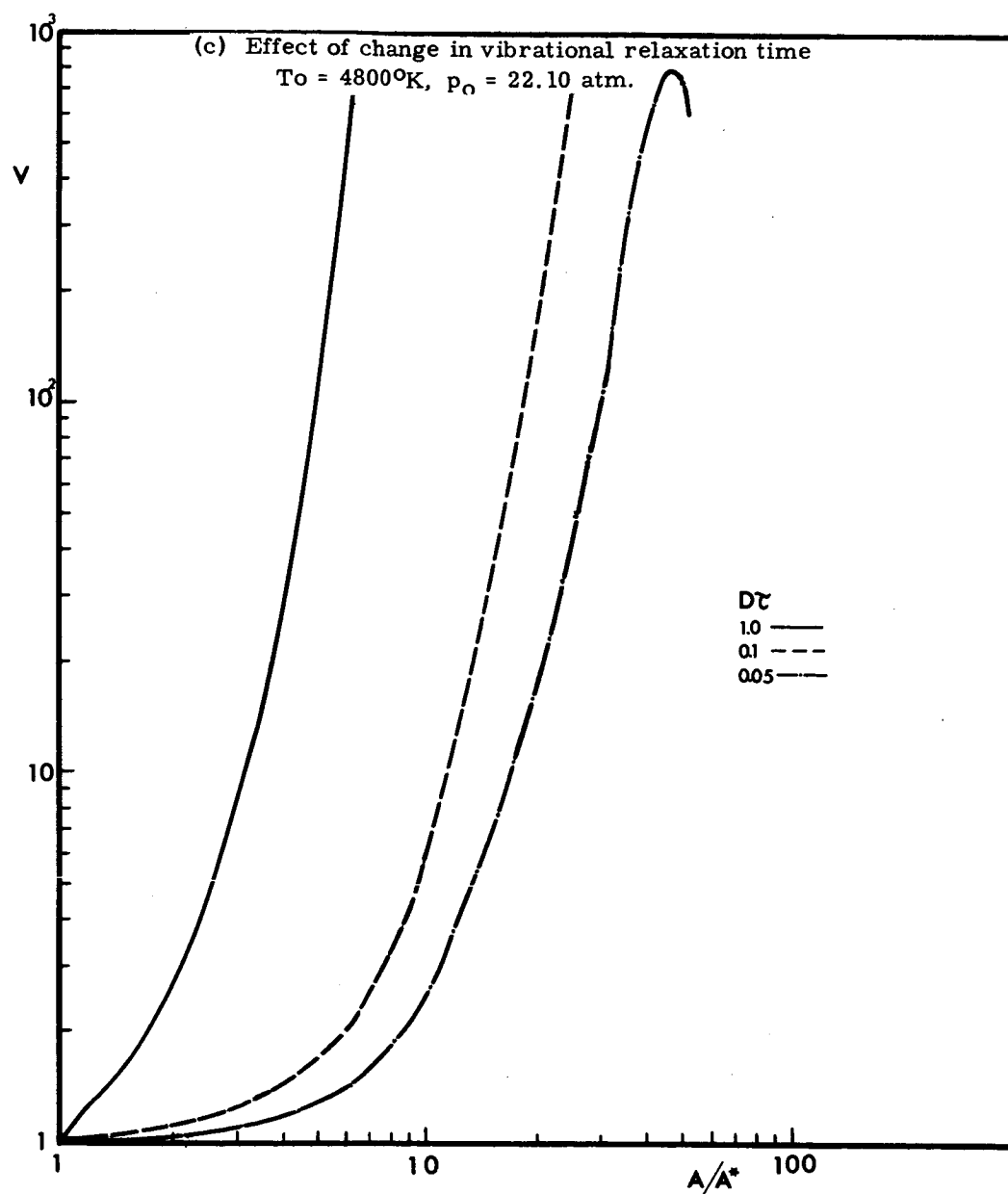


FIG. 11 (continued)

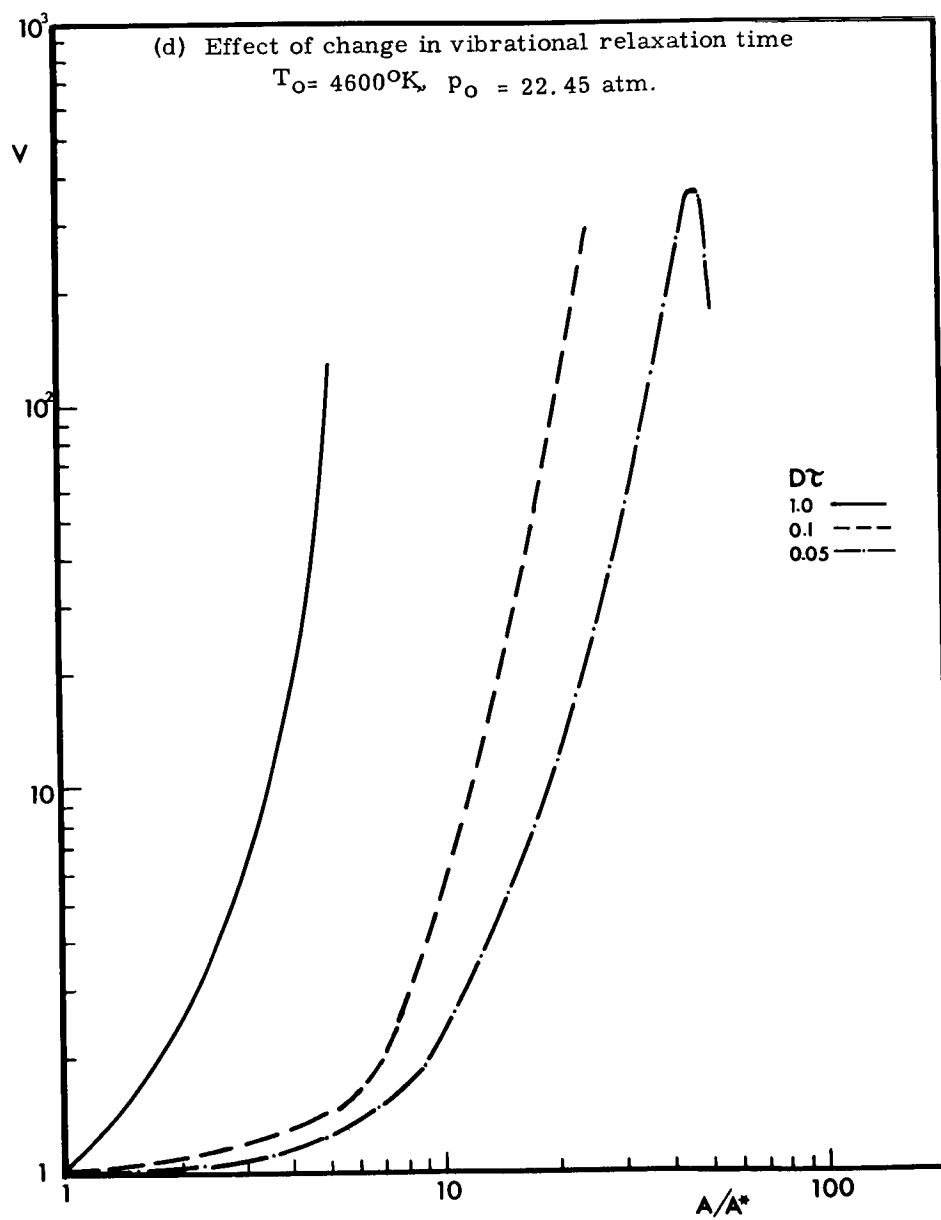
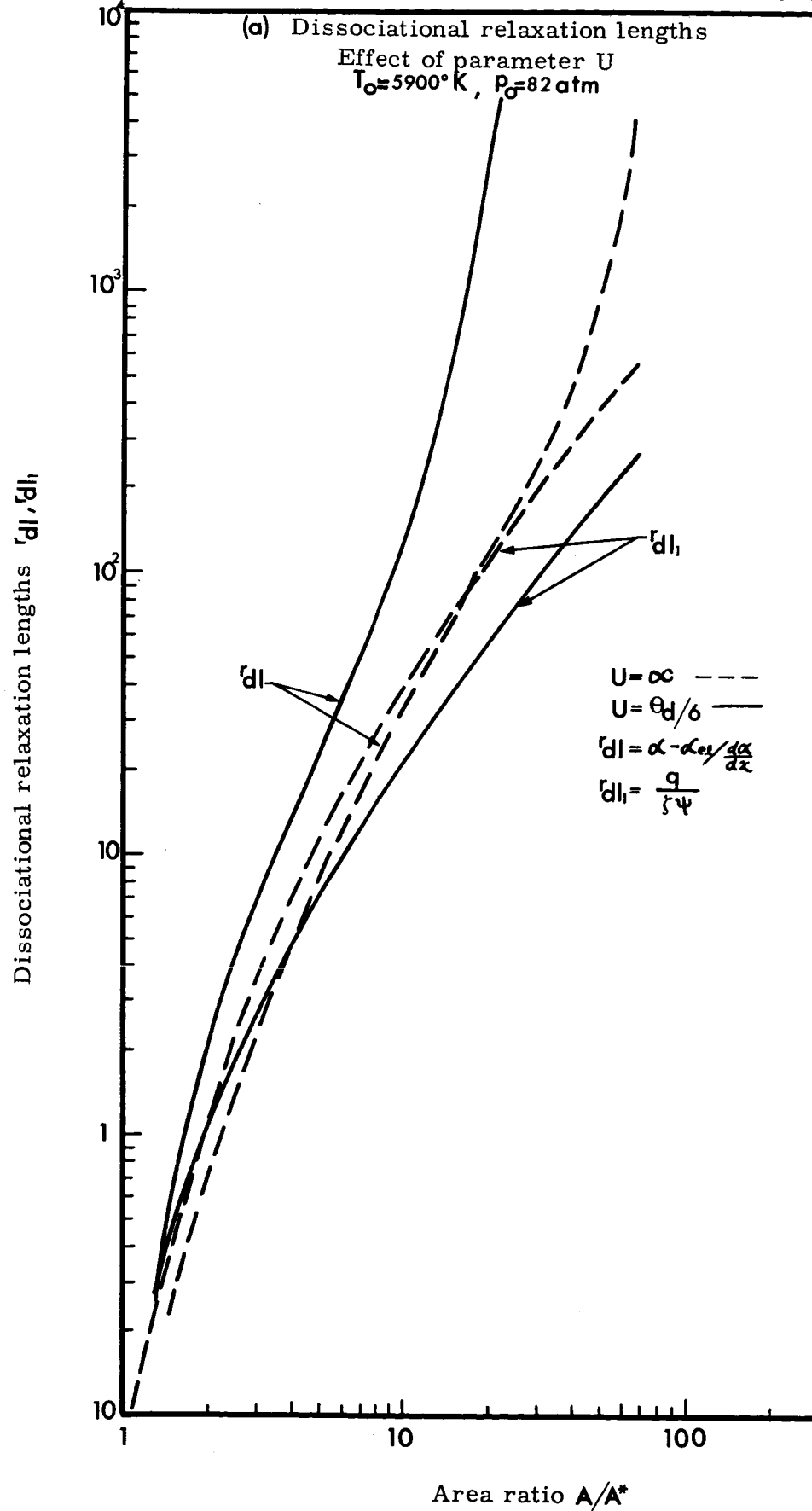


FIG. 11 (continued)

Fig. 12 VARIATION OF RELAXATION LENGTHS ALONG THE NOZZLE



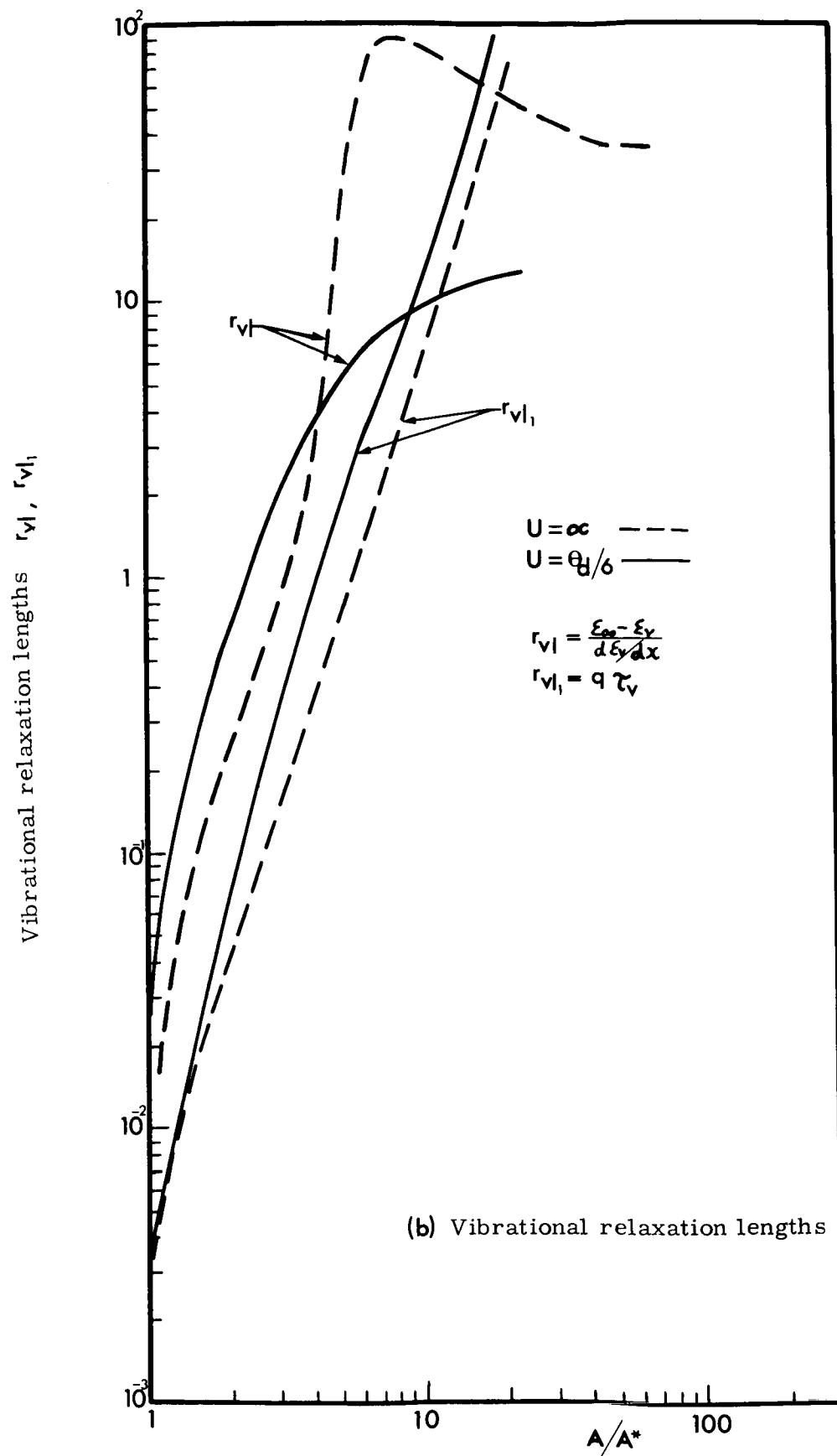


FIG. 12 (continued)

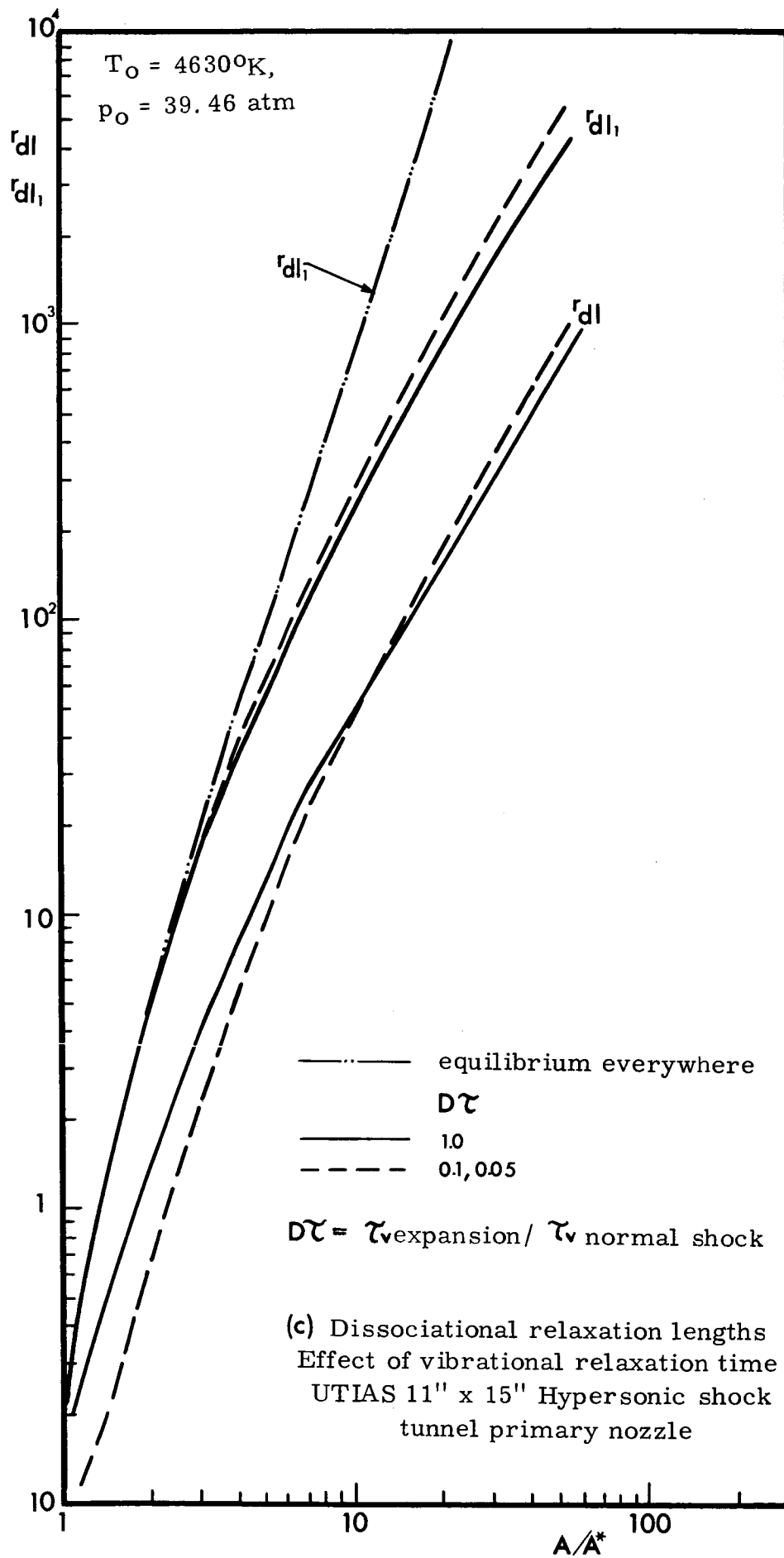


FIG. 12 (continued)

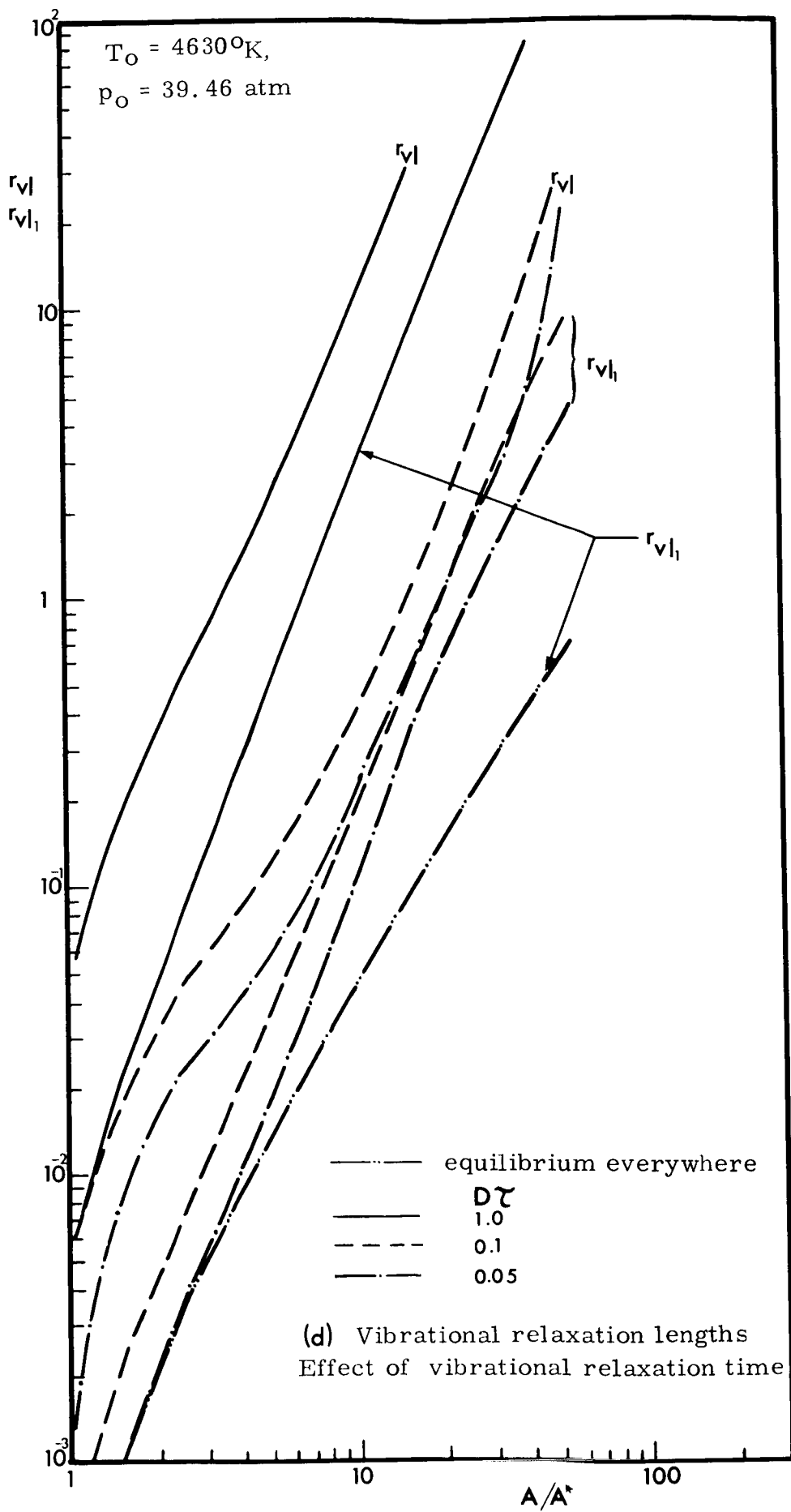


FIG. 12 (continued)

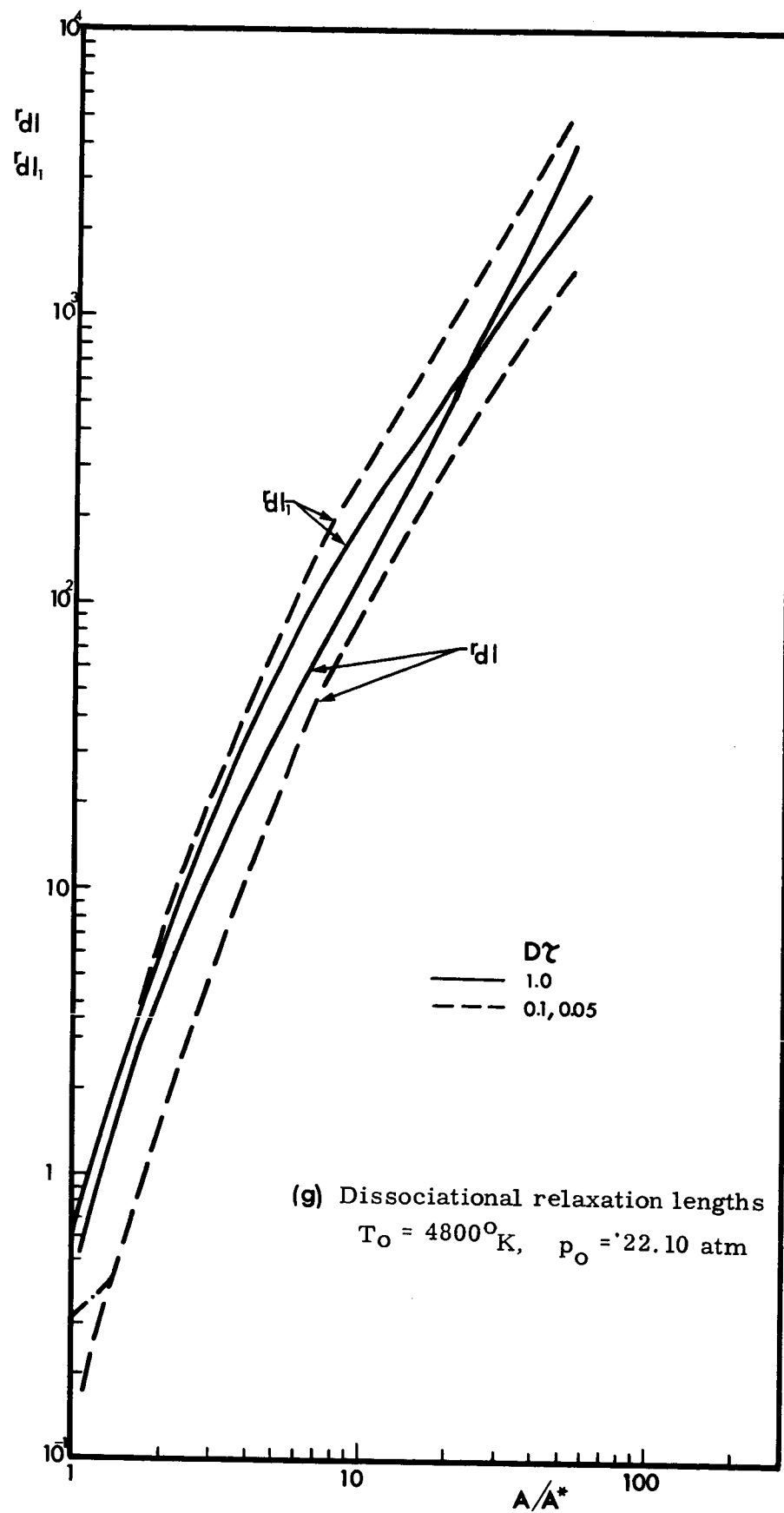


FIG. 12 (continued)

